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Low-Energy Inelastic Atomic Collisions*

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An approximation method is described which is useful for finding inelastic collision cross sections for atomic collisions at energies above about 1 electron volt near threshold. The method uses classical paths for the atoms and the distance of closest approach which is determined from known interatomic forces. The method is applied to the problem of finding the ionization cross section of helium-helium collisions. The comparison of theory and experiment shows satisfactory results.

INTRODUCTION

At present there does not exist a satisfactory and convenient method for low-energy inelastic atomic collisions, that is, a method for the almost adiabatic region. It is well known that the Born approximation applies only when the energy of collision is much larger than the interaction energy between the colliding systems. Furthermore it is required that the collision time be much smaller than the characteristic time of the atoms which is usually taken as $h/\Delta E$.

Now at energies of the order of an electron volt the path of an atom or molecule can be considered as classical since its de Broglie wavelength is of the order of 10^{-9} or 10^{-10} cm, while molecular dimensions are at least 10^{-8} cm. This fact has led to the semiclassical theories of Gaunt[1] and Mott[2] who both use time-dependent perturbation theory with the simplification that $vt=z$. Here v is the velocity of encounter and z is the distance along the zero impact parameter line. This means that the path of the atom or molecule is a straight line. This of necessity is true only at energies much larger than the interaction energy between the colliding systems. If we are interested in a theory for energies near threshold where trajectories are not straight lines, we must devise another theory.

ALMOST ADIABATIC CROSS SECTION

From time-dependent perturbation theory we have for the amplitude of the final state[3]

$$a_{fi}(t)=\frac{1}{i\hbar}\int_{-\infty}^{t}V_{fi}(t')\exp\left[i\left(\frac{E_f-E_i}{\hbar}\right)t'\right]dt',$$

where V_{fi} is the matrix element of the perturbation energy between the initial state i and the final state f. Suppose the perturbation starts at $t=0$ and then decays very slowly because the atom or molecule has lost energy and is moving away very slowly. Then

$$\begin{aligned}a_{fi}(\infty)&=\frac{i}{i\hbar}\int_{0}^{\infty}V_{fi}(t')\exp\left[i\left(\frac{E_f-E_i}{\hbar}\right)t'\right]dt'\\&=\exp\left[\frac{i(E_f-E_i)t}{\hbar}\right]\frac{V_{fi}}{E_i-E_f}\Bigg|_0^{\infty}\\&\quad-\frac{1}{E_i-E_f}\int_0^{\infty}\frac{\partial V_{fi}}{\partial t'}\exp\left[i\left(\frac{E_f-E_i}{\hbar}\right)t'\right]dt'.\end{aligned}$$

Suppose we express the decay of V_{fi} as

$$V_{fi}=V_{fi}(0)e^{-\alpha t};$$

then

$$a_{fi}(\infty)=\frac{V_{fi}(0)}{E_f-E_i}+\frac{V_{fi}(0)}{E_f-E_i}\left[\frac{\alpha^2}{\alpha^2+\omega^2}-\frac{i\alpha\omega}{\alpha^2+\omega^2}\right],$$

where

$$\omega=(E_f-E_i)/\hbar.$$

For a slow collision, $\omega\gg\alpha$ and

$$a_{fi}(\infty)=\frac{V_{fi}(0)}{E_f-E_i}-i\frac{V_{fi}(0)}{E_f-E_i}\left(\frac{\alpha}{\omega}\right),\tag{1}$$

$$|a_{fi}(\infty)|^2\cong|V_{fi}(0)|^2/(E_f-E_i)^2.$$

Our next step is the choice of the distance between the colliding systems at which one can say that the collision has started. Our approximation is to choose the distance of closest approach as corresponding to time zero. This is because $V_{fi}(R)$ is largest at the distance of closest approach and falls off very rapidly with distance from this point.

If we take R to be the distance of closest approach, then the cross section for a process where the final state is discrete and no photons are involved is

$$\sigma=\int d\sigma=2\pi\int_0^{\infty}|a_{fi}(R)|^2p\,dp,\tag{2}$$

where p is the impact parameter. The relation between p and R is

$$1=\frac{p}{R}+\frac{U(R)}{\frac{1}{2}\mu v^2}=\frac{p}{R}+\frac{U(R)}{E_{\text{rel}}}.\tag{3}$$

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[1] J. A. Gaunt, Proc. Cambridge Phil. Soc. **23**, 732 (1927).

[2] N. F. Mott, Proc. Cambridge Phil. Soc. **17**, 553 (1931).

[3] See, for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955).

Here $U(R)$ is the interaction energy between the molecules or atoms.

If the final state is a continuous one, we need the number of final states. For example, in the ionization of a molecule by another the number of states will be

$$P_e^2 dP_e d\Omega_e/(2\pi\hbar)^3$$

(here we use a box of unit length), P_e is the electron momentum, and $d\Omega_e = 2\pi \sin\theta_e d\theta_e$ is the usual solid angle. The cross section will be calculated in the center-of-mass system and the differential cross section will be

$$d\sigma = 2\pi \int_{\mathrm{M}0}^{\infty} dF(R) p dp, \tag{4}$$

where

$$dF(R) = |a_{fi}(\infty)|^2 P_e^2 dP_e d\Omega_e/(2\pi\hbar)^3,$$

$$= \frac{|V_{fi}(R)|^2}{(I+P_e^2/2m)^2} \frac{P_e^2 dP_e d\Omega_e}{(2\pi\hbar)^3}, \tag{5}$$

where I is the ionization energy. We are neglecting differences in the interaction energy of the molecule between ionized and un-ionized states relative to I. To find the total cross section, we integrate over solid angle $d\Omega_e$ and dP_e. The limits of P_e are 0 to $(P_e)_{\max}$. $(P_e)_{\max}$ is given approximately by

$$[(P_e)_{\max}]^2/2m \cong E_{\mathrm{rel}} - I,$$

which is the energy available in the center-of-mass reference frame after ionization. For this condition the electron carries off most of the energy.

In a particular application it is superior to use

$$U(R) = \text{const } e^{-\text{const}\times R},$$

rather than to use the repulsive part of a Lennard-Jones potential. The reason for this is that at high energies one molecule essentially goes through another with the impact parameter p equal to the distance of closest approach. Under the latter condition our integrals will diverge. The trajectories will be straight lines and our method will not be useful. If the relative energy of collision is an appreciable fraction of $U(0)$, then other methods should be used. If, however, we are dealing with an ion colliding with a neutral structure the latter difficulty would not exist.

APPLICATION TO IONIZING COLLISIONS OF HELIUM-HELIUM

Helium appears to be a good choice for calculation because of its simple electronic structure. Also we have the interatomic interaction energy[4,5]:

$$U(R) = 577.4 e^{-4.40R} \text{ electron volts.}$$

There is only one disadvantage in the case of helium. The interaction energy for small R is only about 500 electron volts. Consequently we shall limit our calculations to energies of the order of 100 ev in the center-of-mass reference frame.

If we call the beam atom A and the target atom B, we have for the perturbation energy:

$$V = \frac{4e^2}{R} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} + \frac{e^2}{r_{14}} + \frac{e^2}{r_{24}} - \frac{2e^2}{A_3} - \frac{2e^2}{A_4} - \frac{2e^2}{B_1} - \frac{2e^2}{B_2},$$

where r_{ij} is the distance between electrons i and j and A_i or B_i is the distance from electron i to nucleus A or B. Electrons 1 and 2 are assigned to nucleus A and 3 and 4 to nucleus B. For the state functions we shall use atomic functions which are products of hydrogenic functions. For simplicity we do not use symmetrized molecular functions. Thus, for the initial state we have

$$\psi_i = \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \pi^{-\frac{1}{2}} \exp\left(-\frac{Z}{a_0}A_1\right) \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \pi^{-\frac{1}{2}}$$
$$\times \exp\left(-\frac{Z}{a_0}A_2\right) \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \pi^{-\frac{1}{2}} \exp\left(-\frac{Z}{a_0}B_3\right)$$
$$\times \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \pi^{-\frac{1}{2}} \exp\left(-\frac{Z}{a_0}B_4\right), \tag{6}$$

where $Z = 27/16$ and a_0 is the radius of the first Bohr orbit of hydrogen. For the final state with an A electron missing, we take

$$\psi_f \cong \frac{1}{\sqrt{2}} \left[\exp\left(\frac{i}{\hbar}\mathbf{P}_{e1}\cdot\mathbf{A}_1\right) \left(\frac{Z}{a_0}\right)^{9/2} \pi^{-\frac{3}{2}} \right.$$
$$\times \exp\left(-\frac{Z}{a_0}(A_2+B_3+B_4)\right) + \exp\left(\frac{i}{\hbar}\mathbf{P}_{e2}\cdot\mathbf{A}_2\right)$$
$$\left. \times \left(\frac{Z}{a_0}\right)^{9/2} \pi^{-\frac{3}{2}} \exp\left(-\frac{Z}{a_0}(A_1+B_3+B_4)\right) \right]. \tag{7}$$

The normalization factor is almost $1/\sqrt{2}$ because the overlap between the two functions in ψ_f is very small (it involves the integral $Re^2 I_1/4$, which we evaluate later). For the removed electron we have to use a simple plane wave which is normalized in a box unit length.

Using the above functions, we find for the matrix element

$$V_{fi} = \sqrt{2}[I_1 - 2I_2 - 2I_5 + RI_1(\tfrac{1}{2}I_3 - \tfrac{3}{2}I_4)], \tag{8}$$

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[4] This potential is an approximation of the author's potential taken from Hirshfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954).

[5] P. Rosen, J. Chem. Phys. 18, 1182 (1950).

where

$$I_1=\frac{4}{R}\frac{e^2}{\pi^{\frac{1}{2}}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\int \exp\left(-\frac{i\mathbf{P}_e\cdot\mathbf{A}_1}{\hbar}\right)\exp\left(-\frac{Z}{a_0}A_1\right)d\tau_1,$$

$$I_2=\frac{e^2}{\pi^{\frac{3}{2}}}\left(\frac{Z}{a_0}\right)^{9/2}\int\int\frac{1}{r_{13}}\exp\left(-\frac{i\mathbf{P}_e\cdot\mathbf{A}_1}{\hbar}\right)$$

$$\times\exp\left(-\frac{ZA_1}{a_0}\right)\exp\left(-\frac{2Z}{a_0}B_3\right)d\tau_1 d\tau_3,$$

$$I_3=\left(\frac{Z}{a_0}\right)^6\frac{1}{\pi^2}\int\int\frac{1}{r_{23}}\exp\left(-\frac{2Z}{a_0}A_2\right)$$

$$\times\exp\left(-\frac{2Z}{a_0}B_3\right)d\tau_2 d\tau_3,$$

$$I_4=\left(\frac{Z}{a_0}\right)^3\frac{1}{\pi}\int\frac{1}{A_3}\exp\left(-\frac{2Z}{a_0}B_3\right)d\tau_3,$$

$$I_5=\frac{e^2}{\pi^{\frac{1}{2}}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\int\frac{1}{B_1}\exp\left(-\frac{i\mathbf{P}_e\cdot\mathbf{A}_1}{\hbar}\right)\exp\left(-\frac{Z}{a_0}A_1\right)d\tau_1.$$

All the integrals except I_2 and I_5 can easily be evaluated. Both I_3 and I_4 are known from the treatment of the hydrogen molecule. We find

$$I_1=32e^2\pi^{\frac{1}{2}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}}\Big/\left\{\left[\left(\frac{Z}{a_0}\right)^2+\left(\frac{P_e}{\hbar}\right)^2\right]^2 R\right\}, \tag{9}$$

$$I_3=\frac{1}{R}\left\{1-\exp\left(-\frac{2ZR}{a_0}\right)\left[1+\frac{11}{8}\frac{ZR}{a_0}+\frac{3}{4}\left(\frac{ZR}{a_0}\right)^2+\frac{1}{6}\left(\frac{ZR}{a_0}\right)^6\right]\right\}, \tag{10}$$

$$I_4=\frac{1}{R}\left\{1-\exp\left(-\frac{2Z}{a_0}R\right)\left(1+\frac{Z}{a_0}R\right)\right\}. \tag{11}$$

Because of the difficulty of evaluating I_2, we shall approximate as follows:

$$I_2\cong\frac{e^2}{\pi^{\frac{3}{2}}}\left(\frac{Z}{a_0}\right)^{9/2}\int\frac{1}{B_1}\exp\left(-\frac{i\mathbf{P}_e\cdot\mathbf{A}_1}{\hbar}\right)$$

$$\times\exp\left(-\frac{Z}{a_0}A_1\right)d\tau_1\int\exp\left(\frac{-2ZB_3}{a_0}\right)d\tau_3,$$

or

$$I_2\cong I_5.$$

Collecting results, we have

$$|V_{fi}|^2=\frac{2048e^4\pi(Z/a_0)^5}{[(Z/a_0)^2+(P_e/\hbar)^2]^4}$$

$$\times\frac{\left\{\exp\left(-\frac{2ZR}{a_0}\right)\left[1+\frac{1}{8}\frac{ZR}{a_0}-\frac{3}{4}\left(\frac{ZR}{a_0}\right)^2-\frac{1}{6}\left(\frac{ZR}{a_0}\right)^3\right]\right\}^2}{R^2}. \tag{12}$$

TABLE I. The ionization cross section of helium-helium collisions *versus* energy and comparison with experiment.

E_{relative}(ev)	E_{lab}(ev)	σ(A^2)	σ_{Rostagni}(A^2)
24.46(=I)	48.92	0	...
40	80	1.10×10^{-2}	0.57×10^{-2}
50	100	2.09×10^{-2}	0.95×10^{-2}
60	120	2.85×10^{-2}	1.51×10^{-2}
70	140	3.42×10^{-2}	2.27×10^{-2}
80	160	3.85×10^{-2}	3.12×10^{-2}
90	180	4.17×10^{-2}	3.78×10^{-2}
100	200	4.37×10^{-2}	4.00×10^{-2}

For the total cross section for ionization we find

$$\sigma=\frac{8192e^4(Z/a_0)^7m^2\hbar^5}{(2mI)^{9/2}}f(\epsilon)\int_0^\infty g\left(\frac{ZR}{a_0}\right)pdp, \tag{13}$$

where

$$f(\epsilon)=\int_0^{\sqrt{(\epsilon/I)}}\frac{x^2dx}{(x^2+1)^2(x^2+a^2)^4}$$

and

$$g\left(\frac{ZR}{a_0}\right)=\frac{1}{(ZR/a_0)^2}\left\{\exp\left(-\frac{2ZR}{a_0}\right)\times\left[1+\frac{ZR}{8a_0}-\frac{3}{4}\left(\frac{ZR}{a_0}\right)^2-\frac{1}{6}\left(\frac{ZR}{a_0}\right)^3\right]\right\}^2.$$

Here

$$a^2=\hbar^2Z^2/(2mIa_0^2),\quad \epsilon=E_{\text{rel}}-I.$$

Because of $f(\epsilon)$, when the energy of atom A relative to atom B is the ionization energy, the cross section will be zero. Because atom A has the same mass as B, the threshold energy in the laboratory reference frame will be $2I$.

In Table I we have tabulated calculated results and compared with the results of Rostagni[6] where possible. The agreement between experiment and theory is satisfactory. Furthermore it is extremely difficult to obtain experimental results below 100 electron volts in the laboratory reference frame. Consequently a theory near threshold is a necessity if one requires a knowledge of cross sections for the thermal ionization that takes place in a shock wave, for example.

Another interesting aspect of this work is the possibility of computing chemical reaction rates at high temperatures by computing the cross sections. If these results are then put into the form of the Eyring theory, activation energies may be computed.

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[6] A. Rostagni, Nuovo cimento **11**, 621 (1934).