Theoretical cross sections for collisional angular momentum transfer in atomic Rydberg states

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Abstract. A simple semiclassical model already proposed by Gersten and Omont is used for the calculation of the angular momentum transfer in collisions of hydrogenic Rydberg states with rare gases. The model, which uses a Fermi pseudopotential, is applied to the quenching of \((n = 8−14)\) D states of Na by He and Ne, and is found to be in rough agreement with experiment when \(n \geq 10\). The main new fact to be noted is the prediction that all \(L\) (angular momentum) changing cross sections have the same order of magnitude, whatever the final value of \(L\). The physical basis of the model is discussed. It is simply shown that the Fermi pseudopotential and binary encounter methods are unable to predict slightly inelastic transfer cross sections (\(\Delta E\) greater than a few tens of cm\(^{-1}\)).

1. Introduction

Experimental studies of the quenching of Na \(n^2D_{5/2}\) for \(n = 5−15\) in collisions with rare gases have recently been performed (Gallagher et al 1975, 1977a,b). The measured cross sections show an unexpected dependence on the principal quantum number \(n\): up to \(n \sim 10\) they increase as \(n^4\) (i.e. like the geometrical cross sections), then, when \(n \geq 10\), decrease.

This strange behaviour has been theoretically explained by Olson (1977). His model, however, is not entirely satisfactory: indeed he assumes that the quenching is mainly due to \(n^2D_{5/2}−n^2F_{5/2}\) transfer and neglects rotational coupling between molecular states; that allows him to reduce the problem to a two-state system. However, neither the first nor the second hypothesis seems to be justified.

At the same time, Gersten (1976) has developed a semiclassical approach using a Breit–Fermi pseudopotential for the excited-atom–rare-gas interaction. His model applied to the cases where \(n = 4−7\) is found in semi-quantitative agreement with existing experiments (Gallagher et al 1975). However, he must use the strong-collision approximation to treat low impact parameter collisions and that is the most evident deficiency of the method.

For fairly excited states, however, one may hope that neither the strong-collision approximation nor a close-coupling calculation are needed and that a semiclassical calculation carried to the first order of perturbation only should be sufficient. In addition the Fermi pseudopotential should be the more justified the slower and more loosely bound the valence electron, i.e. the larger \(n\).
Now this Fermi pseudopotential leads to quite tractable calculations and allows us to take into account the complete set of states actually coupled by the collisions. Thus Gersten's model seems appropriate to the theoretical treatment of the quenching of Rydberg states and this was recently done by Omont (1977). However, in order that the calculations remain analytical up to the end, he must use some approximations: WKB wavefunctions; and discrete sums replaced by continuous sums. These are justified for very highly excited states, but their range of validity is indistinct. It is interesting to note that this yields results identical to those obtained from the semi-quantal binary encounter theory (Flannery 1970).

In this work we have applied Gersten's model to the quenching of atomic \((n = 8–14)\) D states. We did not use Omont's approximations and as a consequence were obliged to do brute force numerical calculations. The advantages are the following:

(i) Several intermediate results (in particular values of the cross sections for the transfer of a given quantity of angular momentum) can be derived (cf table 2).

(ii) The comparison of our results with Omont's can give an idea about the range of validity of his approximations (cf equation (9) and figure 1).

(iii) At present, experiments have been done only on relatively low excited states \((n \leq 15)\) for which the applicability of Omont's approximations is doubtful. However, the physical model in itself may nevertheless be justified. Hence our more rigorous treatment enables us to test the model experimentally (cf table 1 and figure 1).

We first briefly survey the principle of the method and discuss the results, which are found to be in rough agreement with existing experiments. Perhaps the most important result of this paper is the prediction that all angular momentum transfers for a shell of given principal quantum number should have the same probability whatever the final value of the angular momentum.

Some physical remarks relative to the model are also presented; in particular, it is shown that the pseudopotential should not be used to describe collisions which involve a variation of the internal energy of the atom larger than a few tens of \(\text{cm}^{-1}\), independent of the degree of excitation of the atom; for these a fully quantum theory is needed.

2. Principle of the model and derivation of the cross sections

We shall use a semiclassical method with a Breit–Fermi pseudopotential for the interaction between the Rydberg and rare-gas atoms:

\[
V(R, r) = 2\pi a_0^2 (r - R) \quad (\text{au})^\dagger
\]

where \(R\) and \(r\) are, respectively, the locations of the rare-gas atom and valence electron, the origin being taken at the centre of the Rydberg atom; \(a\) is the zero-energy scattering length of electrons by the rare gas.

We expand the state of the valence electron on a hydrogenic basis \(|nlm\rangle\) and neglect exchange effects, fine and hyperfine structures, and all other interactions with the core. The perturbing atom is supposed to move classically along a straight-line trajectory with a constant velocity \(v\), at the impact parameter \(b\):

\[
R = b + vt.
\]

* In all the following we usually use the atomic units system: \(\epsilon = \hbar = m = a_0 = 1\).
From the time-dependent Schrödinger equation we get, to the first order of perturbation theory, the transition probability

\[ P_{n \rightarrow m} \propto (2\pi a)^2 \left| \int_{-\infty}^{+\infty} \psi_{n,m}^*(R(t)) \psi_{n,m}(R(t)) \exp[i(E_{n,m} - E_m)t] dt \right|^2 \]  

(2)

where

\[ \psi_{n,m}(R) = \langle R | n,m \rangle = N_n R_n(R) Y_{l,m}(R/R) \]

with

\[ R_n(R) = \exp(-R/n)(2R/n)^{l+1/2} \]

and \( L^{(2l+1)}_{n+l} \) is a generalised Laguerre polynomial as defined by Bethe and Salpeter (1957)

\[ N_n = -\left( \frac{(2/n)^3(n - l - 1)!}{2n(n + l)!^3} \right)^{1/2}. \]

\( E_{nl} \) is the eigen-energy of the state of the excited atom which corresponds to the hydrogenic state \( |nlm\rangle \). The integrals are computed using the simple Simpson algorithm.

We have verified that the factor \( \exp[i(E_{n,m} - E_m)t] \) has no effect on the transition probabilities once the energetic separation \( \Delta E \) is such that \( \Delta E/v \approx 0.5/n \) au (cf Omont 1977; equations (3)-(8)); on the other hand, when \( \Delta E/v \approx 0.5/n \), the transition probabilities are considerably reduced. That allows us to make some approximation. Indeed, in the case of the Na \((n^2D_{5/2}) + X\) thermal collisions (with \( X = \text{He, Ne} \)) we have \( v \approx 5 \times 10^{-4} \) au. For \( n \approx 10 \) the critical value \( \Delta E_c = 0.5v/n \) is about \( \Delta E_c \approx 2.5 \times 10^{-5} \) au = 5 cm\(^{-1}\). Now:

(i) In the case of Na, the 8D–8F separation is 2.8 cm\(^{-1}\). For \( n \geq 8 \) this justifies our previous assumptions which lead to the neglect of fine and hyperfine structures; in addition we will also completely neglect the energetic interval between \( nD \) and \( nF, G, H, \ldots \) levels, thus dividing the computation time for one given collision by two.

(ii) Also, the Fermi first-order shift \( 2\pi a|\psi(R)|^2 \) for \( n \approx 10 \) is about a few hundredths of cm\(^{-1}\) and will be neglected.

(iii) In the case of Na, apart from the \( nF, G, H, \ldots \) levels, it is the \((n + 1)P\) which is the closest to the \( nD \); as the 14D–15P interval is about 10 cm\(^{-1}\), for \( n > 14 \) we may neglect the contribution to the quenching of transfers outside the \( nD, F, G, H, \ldots \) shells.

From equation (2) we get the cross sections by first averaging over all orientations \( \Omega \) of \( b \), integrating over \( b \) and averaging over the Maxwell distribution of \( v \). The first step requires we also average over the magnetic quantum numbers. We obtain easily (Gersten 1976):

\[ \overline{\sigma}_{n \rightarrow m}(b, v) = \int \frac{1}{2l + 1} \sum_{m'} (P_{n \rightarrow m/m'}(b, v, \Omega)) \frac{d\Omega}{4\pi} \]

\[ = \frac{2\pi a^2}{2l + 1} N_n^2 N_{n'}^2 \]

\[ \times \left( \sum_{\mu} |Y_{l,\mu}(\pi/2, 0) Y_{l',\mu}(\pi/2, 0)|^2 \left| \int_0^{\pi/2} R_{n}(R) R_{n'}(R) \exp[i(\mu' - \mu)\phi] d\phi \right|^2 \right) \]

(3)

with \( R = (b^2 + v^2 t^2)^{1/2} \) and \( \tan \phi = vt/b \).
Secondly the cross sections $\sigma_{nl\rightarrow nl'}(v)$ for a given relative velocity $v$ is given by

$$\sigma_{nl\rightarrow nl'}(v) = \int_0^\infty 2\pi b \, P_{nl\rightarrow nl'}(b, v) \, db.$$  

(4)

It is straightforward, but important, to realise that we have

$$\sigma_{nl\rightarrow nl'}(v) = (a/v)^2 \, A_{nl\rightarrow nl'},$$  

(5)

where $A_{nl\rightarrow nl'}$ involves only the wavefunctions of the excited atom, which are hydrogenic in our case. All the dependence on the kinds of atoms considered is contained in the factor $(a/v)^2$.

### 3. Results and comparison with existing experimental data

At present the only information we get from experiment is the quenching rate. The corresponding cross sections are obtained by summing all the processes which contribute to the quenching; in the case of the nD states we have

$$\sigma_{nD}(v) = \sum_{i=3}^{n-1} \sigma_{ni\rightarrow n'i}.$$  

(6)

Now we have to average over the thermal velocity. However, as is well known, the quantity we get from experiment and usually called 'cross section' is not $\langle \sigma_{nD}(v) \rangle$, but $\langle \sigma_{nD}(v) \rangle \langle v \rangle$ (where brackets mean average over $v$).

From (5) and (6) we obtain the 'average cross section'

$$\langle \sigma_{nD}(v) \rangle \langle v \rangle = a^2 \frac{1}{\langle v \rangle} \left( \sum_{i=3}^{n-1} A_{nD\rightarrow n'i} \right).$$  

(7)

If we take a Maxwell–Boltzmann distribution for the relative velocity we get easily

$$\langle \sigma_{nD}(v) \rangle \langle v \rangle = \frac{3}{2} \frac{a^2}{\langle v^2 \rangle} \left( \sum_{i=3}^{n-1} A_{nD\rightarrow n'i} \right) = \frac{M^* a^2}{2kT} \left( \sum_{i=3}^{n-1} A_{nD\rightarrow n'i} \right)$$  

(7')

where $M^*$ is the reduced mass of the Rydberg-atom–perturbing-atom system. We have applied our final formula to the quenching of nD states of Na by He and Ne, for which experimental data exist (Gallagher et al 1977b). Application to other kinds of collisional partners is trivial: one has just to change the constant factor $a^2/\langle v^2 \rangle$. According to Gallagher’s experimental conditions we took $T = 430$ K. For the electron scattering length we used the values (Massey and Burhop 1969) $a(\text{He}) = 1.19$ au; $a(\text{Ne}) = 0.24$ au.

The calculations were carried out for $8 \leq n \leq 14$: for $n \leq 8$ the perturbation approach breaks down completely: for $n > 14$ numerical-analysis problems appear, e.g. overflow in the computation of the Laguerre polynomials which can be removed by using recurrence relations existing for the Laguerre polynomials, but anyway the computation time is raised approximately as $n^4$.

Our results are shown in table 1 and figure 1. We see that there is a semi-quantitative agreement with the experimental measurements. In the case of He, the strong discrepancy for $n = 8$ and $n = 9$ should be explained by the fact that the perturbation treatment is not valid. On the other hand, it must be noted that the agreement
Table 1. Comparison of our theoretical results with experiment for the quenching of Na \(nD\) states by He and Ne. (Values of the cross sections are in \(\text{Å}^2\).) \(\bar{P}\) is obtained by dividing the velocity averaged cross sections by the geometrical cross sections; that gives an order of magnitude for the transition probability; perturbation theory is justified only when \(\bar{P} \ll 1\); this is not the case for He \(n = 8\) and \(n = 9\).

<table>
<thead>
<tr>
<th>Level (theory)</th>
<th>Quenching cross section ((10^3 \text{Å}^2))</th>
<th></th>
<th>Quenching cross section ((10^3 \text{Å}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Our calculation (equation (7))</td>
<td>Experiment (Gallagher et al)</td>
<td>Our calculation (equation (7))</td>
</tr>
<tr>
<td>6D</td>
<td>0.38 (7)</td>
<td>0.36 (7)</td>
<td>0.38 (7)</td>
</tr>
<tr>
<td>7D</td>
<td>0.81 (10)</td>
<td>0.81 (10)</td>
<td>0.81 (10)</td>
</tr>
<tr>
<td>8D 0.96</td>
<td>6.93</td>
<td>1.05 (20)</td>
<td>0.12</td>
</tr>
<tr>
<td>9D 0.45</td>
<td>5.15</td>
<td>1.04 (20)</td>
<td>0.057</td>
</tr>
<tr>
<td>10D 0.22</td>
<td>3.93</td>
<td>2.2 (8)</td>
<td>0.028</td>
</tr>
<tr>
<td>11D 0.12</td>
<td>3.00</td>
<td>1.85 (20)</td>
<td>0.015</td>
</tr>
<tr>
<td>12D 0.065</td>
<td>2.37</td>
<td>1.69 (30)</td>
<td>0.0082</td>
</tr>
<tr>
<td>13D 0.038</td>
<td>1.93</td>
<td>1.65 (30)</td>
<td>0.0050</td>
</tr>
<tr>
<td>14D 0.023</td>
<td>1.59</td>
<td>1.33 (20)</td>
<td>0.0029</td>
</tr>
<tr>
<td>15D</td>
<td>1.38 (20)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the case of Ne is somewhat fortuitous: indeed as will be shown below, the scattering-length approximation is not well justified in that case and the true cross sections (see e.g. Massey and Burhop 1969, p 555) should be two or three times larger; for the same reason, the application of our model to the case of quenching by heavier rare gases is even less justified (the Ramsauer–Townsend effect appears) apart from

**Figure 1.** Quenching of the \(nD\) states of Na by He and Ne at 430 K: semi-logarithmic plot of the velocity averaged cross sections \(\langle \sigma (v^2) \rangle \langle t \rangle \) against the principal quantum number \(n\). Experiment: I, Gallagher et al; theory: ●, this work; Δ, Omont (1977), equation (9); V, Omont (1977), equation (10); +, geometrical cross section \((4\pi \alpha^2)\).
Table 2. Numerical values for the collisional angular momentum transfer from the D states ($L = 2$) inside the $n = 13$ shell. Transfer towards S and P states ($L = 0$ and $L = 1$) has also been calculated assuming the energy intervals D–S and D–P to be zero (as for the intervals D–F, G, H, ...). Also the $\sigma_{2-2}$ cross section has been formally calculated and gives an order of magnitude for the depolarisation processes compared with the quenching ones. The numerical values are given in atomic units assuming $a_0^3$ to be $10^9$ au (see text).

<table>
<thead>
<tr>
<th>Transfer $13L \to 13L$</th>
<th>Cross section</th>
<th>Transfer $13L \to 13L$</th>
<th>Cross section</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \to 0$</td>
<td>48</td>
<td>$2 \to 7$</td>
<td>205</td>
</tr>
<tr>
<td>$2 \to 1$</td>
<td>151</td>
<td>$2 \to 8$</td>
<td>194</td>
</tr>
<tr>
<td>$2 \to 2$</td>
<td>293</td>
<td>$2 \to 9$</td>
<td>184</td>
</tr>
<tr>
<td>$2 \to 3$</td>
<td>283</td>
<td>$2 \to 10$</td>
<td>180</td>
</tr>
<tr>
<td>$2 \to 4$</td>
<td>264</td>
<td>$2 \to 11$</td>
<td>169</td>
</tr>
<tr>
<td>$2 \to 5$</td>
<td>243</td>
<td>$2 \to 12$</td>
<td>166</td>
</tr>
<tr>
<td>$2 \to 6$</td>
<td>225</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

the fact that perturbation theory is absolutely invalid (for Ar the $(a_0/v)^2$ factor is almost ten times that of He, likewise the transition probabilities).

Several other important results appear from our calculations.

(i) As shown in table 2, inside the shell of principal quantum number $n$, all the $\sigma_{nD \to nl'}$ are of the same order of magnitude, whatever $l'$. That invalidates Olson's assumption (Olson 1977). It seems to have been verified experimentally (Gallagher et al 1977a) and is in agreement with a simple physical picture: let us assume that the valence electron of the excited atom is quasi-free and quasi-classical. In a binary encounter collision between this electron and the perturbing atom, we shall see later (§5) that the modulus of the velocity of the electron is practically unchanged, but the direction of this velocity may be changed and that leads to a change in the angular momentum of the excited atom. Now the Fermi pseudopotential implicitly assumes that in the valence-electron–perturbing-atom interaction, only the isotropic S wave is scattered. Since the scattering process of the valence electron by the perturbing atom is isotropic, one understands that the angular momentum transfer occurs towards all possible values.

(ii) In view of the numerical results obtained, one can approximately fit the behaviour of each $\sigma_{nD \to nl'}$ when plotted against $n$ by an $n^{-4}$ scaling law. Such a scaling law is purely empirical, however, it is roughly related to the fact that, from Omont (see below equation (9)), the total quenching cross section $\sigma_{nD}^0$ should approximately behave like $n^{-3}$; as $\sigma_{nD}^0$ is the sum of $n\sigma_{nD \to nl'}$ which have all the same order of magnitude, this ‘order of magnitude’ will behave like $n^{-4}$.

In particular we have approximately

$$\sigma_{nD \to n0}(v) = \sigma_{nD \to n5}(v) \sim (a_0/v)^2 1.4/n^4 \text{ (au)}$$

$$\sigma_{nD \to n1}(v) = \sigma_{nD \to n6}(v) \sim (a_0/v)^2 4.3/n^4 \text{ (au)}$$

$$\sigma_{nD \to n2}(v) = \sigma_{nD \to n7}(v) \sim (a_0/v)^2 8.5/n^4 \text{ (au)}$$

$$\sigma_{nD \to n6}(v) = \sigma_{nD \to n8}(v) \sim (a_0/v)^2 5.5/n^4 \text{ (au)}$$

The first three cross sections do not contribute to the quenching cross section of the D states of Na and, of course, have not been included in the results of table 1.
However, their computing procedure is obviously the same as for the others. Equation (8c) gives an order of magnitude of the depolarisation cross sections.

(iii) Our results are noticeably different from Omont's, who gives

\[ \sigma_{nG}^{(0)}(v) = (a/v)^2 2\pi/n^3 \text{ (au)}. \]  

Figure 1 shows that this deviation decreases as \( n \) increases, as was expected, but the convergence seems rather slow.

In fact most of the deviation should be attributed to the fact that the transfers \( nD \to nl' = 0-2 \) are formally included in Omont's calculations. Indeed, in equation (9), we can remove the contributions of the \( \sigma_{nD \to nl'}(l' = 0-2) \) using the scaling laws (8a,b,c). Then we get

\[ \sigma_{nG}^{(0)}(v) \sim (a/v)^2 (2\pi/n^3 - 14/n^4) \text{ (au)} \]

which somewhat reduces the discrepancy (see figure 1).

(iv) Expression (6) can also be considered as the integral over the impact parameter \( b \) of the function

\[ 2\pi b P_{nG}^0(b, v) = \frac{d\sigma_{nG}^0(v)}{db} \]

\[ \sigma_{nG}^0(v) = \int_0^\infty 2\pi b P_{nG}^0(b, v) db. \] 

The shape of this function is shown in figure 2 where we have \( n = 13 \): it strongly resembles the radial distribution function of the \( nD \) orbitals (both curves have maxima located at the same positions). For any \( n \) this curve has the same basic features, which show that the quenching takes place with the same order of magnitude for all \( b \) smaller than \( 2n^2 \). This last bound corresponds to the apogee of the Bohr–Sommerfeld orbit \( nl \) when \( l \ll n \) and roughly delimits the electronic cloud of the

![Figure 2](image)
atom excited in its $nD$ state. For $b > 2n^2$ the quenching probability falls off very rapidly. It must be noted that the relative contribution of the low impact parameters is small: this is important for the self-consistency of the model since we shall see that the pseudopotential is not valid for small internuclear distances.

Figure 3 shows the shape of $P_{nD}^0(b, v)$. We see that apart from the region of small $b$ (which has no physical significance and contributes little to the cross section) the quenching probability is roughly constant up to $b \sim 2n^2$ where it vanishes. This leads us to have some doubts about the numerical results obtained by Gersten (1976) who cuts off the integration over $b$ when $P_{nD}^0(b, v)$ becomes greater than the statistical ratio $F = (n^2 - 9)/(n^2 - 5)$; he then supposes the collisions to be strong below the cut-off. Now, from the preceding remarks we believe that if there occurs a cut-off, it should be practically at $b \sim 2n^2$. As the 'tail' of the integral should then contribute very little, the obtained cross sections should be of the order of the geometrical cross section, i.e. $\sim 4\pi n^4$ au. However, the values given by Gersten are about four times smaller.

4. Discussion of the model

4.1. Impact-parameter method

In our case, the thermal velocity is about $v \sim 10^{-3}$ au. The momentum of the rare-gas atom $P = Mv$ is about 10 au and the corresponding de Broglie wavelength $\lambda = 2\pi\hbar/P \sim 1$ au; this latter is very small with respect to the impact parameters mainly involved in our collisions. This justifies the classical-trajectory approximation for the rare-gas atom.
On the other hand, the distance $R$ where one will mainly find the valence electron is about $n^2 \text{ au}$; the corresponding momentum and velocity are respectively $p = m v_e \sim 1/n \text{ au}$ and $v_e \sim 1/n \text{ au}$. Thus we see that we have $P \gg p$ and $v \ll v_e$. Under these conditions it can easily be shown (see below) that the classical momentum transfer in a binary encounter collision between the rare-gas atom and the electron is about $p$, hence very small with respect to $P$. This justifies the straight-line trajectory.

4.2. Fermi pseudopotential

Its validity range is not yet cleared up. Indeed several facts are involved.

(i) The excited-atom–rare-gas interaction is described by means of the phaseshifts corresponding to the scattering of a free electron by the rare gas. We then neglect the action of the core during the scattering of the valence electron by the rare gas. This is the ‘impulse approximation’ (Goldberger and Watson 1964). For this to be valid, it has to be noted that the binding energy of the electron need not always be small with respect to the kinetic energy of the incident particle: indeed, in our case, the Coulomb potential of the core does not vary too much over the effective range of the electron–rare-gas interaction. In other words, the ‘force’ due to the core is very small compared to that occurring in the collision of a free electron and a rare-gas atom which is called the ‘quasi-classical binding’ by Goldberger and Watson, and they write the validity condition of the impulse approximation in that case (Goldberger and Watson 1964, p 690) as:

$$\frac{a}{\hbar/(Mv)} \frac{2e^2/R^3}{2m} \frac{h^2}{(Mv^2/2)^2} \ll 1$$

where $m$ is the electron mass, $M$ the mass of the rare-gas atom; $a$, in our case, is of the order of the zero-energy scattering length of the electron by the rare gas. With $a \sim 1 \text{ au}$, $Mv^2/2 \sim \frac{3}{2}kT \sim 2 \times 10^{-3} \text{ au}$, $\hbar/Mv \sim 1 \text{ au}$, we get the condition for the internuclear distance $R$

$$R^3 \gg 10^6 \text{ au}$$

or

$$R \geq 100 \text{ au}.$$  \hfill (11a)

This condition is then very severe and may preclude any use of pseudopotentials based on free-electron scattering parameters to treat collisions involving states $n \leq 10$.

(ii) We have supposed that the scattering-length approximation is valid for the scattering of the quasi-free valence electron by the rare-gas atom. This requires the de Broglie wavelength of the electron to be large with respect to the range of the rare-gas potential, i.e. (Hinckelmann and Spruch 1976):

$$\alpha k/a \ll 1 \text{ au}$$

where $\alpha$ is the rare-gas polarisability and $k$ the wavevector of the electron; quasi-classically $k \sim 1/n$. For $n \sim 10$, we see that the condition is well fulfilled in the case of He ($a = 1.19 \text{ au}$, $\alpha = 1.38 \text{ au}$) but only rather badly in the case of Ne ($a = 0.24 \text{ au}$, $\alpha = 2.663 \text{ au}$) and the heavier rare gases. It is theoretically possible to build pseudopotentials which include the scattering of higher order partial waves (Olson 1977, Omont 1977, equations (2)–(20)), but in practice the resulting computation times are tremendously enhanced.

(iii) Finally the pseudopotential performs a kind of average over the state of the excited atom for the scattering of the valence electron by the rare gas. Knowing whether this procedure is justified is a tricky problem.
From Omont (1977) and Flannery (1970) it seems that the state of the excited atom must be quasi-classical, but no precise limit of validity is stated. Intuitively, however, it is not obvious that such a condition is required if the scattering-length approximation is valid for mostly plane waves which form the wavefunction of the electron in momentum space.

(iv) In conclusion, we should like to say that the shift of the alkaline spectral lines perturbed by rare gases can be explained using a theory the physical basis of which is somewhat similar to ours (Alekseev and Sobel'man 1965, Ivanov 1976). The fact that this yields excellent agreement with experiment helps to accredit our approach.

However, the preceding sections show that obviously the pseudopotential is irrelevant to describe the excited-atom–rare-gas interaction at small internuclear distances. The self-consistency of our approach requires the contribution of low impact parameter collisions to the cross sections to be small; this is true (cf §3 and figure 2).

4.3. *Hydrogenic wavefunctions*

For Na D states, the quantum defect is about 1%. Hence the wavefunctions differ very little from hydrogenic ones.

4.4. *Perturbation treatment*

To be valid, the perturbation treatment must yield a total transition probability which remains small compared to unity. As has been said, and is seen in figure 3, the predicted quenching probability has a constant order of magnitude over the range $0 < b < 2n^2$ (except for very small $b$) for the impact parameter $b$, and is zero for $b > 2n^2$. This order of magnitude will be roughly given by the ratio $\bar{P} = \langle \sigma_{\text{Q}}^0 \rangle / 4\pi n^4$ of the quenching cross section to the geometrical cross section, and is justified only if the small impact parameter collisions (where the transition probability strongly increases) contribute little to the cross section; however, one sees from figure 2 that this is true.

Such 'average transition probabilities' $\bar{P}$ are given in table 1 together with the cross sections. We see that perturbation theory is valid for states with principal quantum number greater than 10.

5. *Extension of the model to the study of inelastic transfers*

The effect of a slight energy difference between the levels coupled by collisions can, in principle, be easily taken into account. As seen in equation (2), at first order of perturbation we have just to keep the factor $\exp(i\Delta E t)$. However, the computing time is considerably enhanced—at least by a factor of two; much more if one takes an average over the thermal velocity (cross sections are no longer $\propto (a/v)^2$).

However, what we want to point out is that the applicability of our model to the study of inelastic collisions is strongly limited: indeed, as will be shown, such collisions occur efficiently at low impact parameters; now as seen above, at small internuclear distances, the pseudopotential is not valid. In fact, consider a classical binary encounter collision between two free particles: one is an electron, which is
light and fast, the other is a rare-gas atom, which is heavy and slow. Their initial momenta are respectively \( p = m v_e \) and \( P = M v \), and we have \( P \gg p, v_e \gg v \). Let \( \Delta E \) be the kinetic energy exchange between the two particles due to the collision. Conservation of energy and momentum of the system (taking into account the above conditions) yields\(^\dagger\)

\[
\Delta E \approx \Delta p \cdot v \sim m v_e v
\]

(13)

where \( \Delta p \) is the momentum variation of the electron. Hence, quasi-classically, for transfer to be possible between two states the energy difference of which is \( \Delta E \), the electron must have an initial velocity at least equal to \( \Delta E/mv \). This requires the impact parameter to be smaller than a given value: indeed we have

\[
\frac{1}{2} m v_e^2 - e^2/R = -R_y/n^2.
\]

(14)

For \( n^2 \gg 1 \), equation (14) leads to

\[
\frac{1}{2} m v_e^2 \approx e^2/R
\]

and \( v_e \geq \Delta E/mv \) implies

\[
R \lesssim 2e^2 m v^2/(\Delta E)^2.
\]

(15)

Now, let \( R_c \) be the lowest limit of the internuclear distance for the pseudopotential to be valid. Then our model is unable to predict collisional transfer cross sections between states of which the energy difference \( \Delta E \) is greater than a limit \( \Delta E_c \). In fact from (15)

\[
R > R_c \implies \Delta E < \Delta E_c \approx (2e^2 m v^2/R_c)^{1/2}.
\]

(16)

To give an order of magnitude, let us take \( R_c \sim 100 \) au. With \( 2v^2 \sim 10^{-6} \) au one obtains

\[
\Delta E_c \sim 10^{-4} \text{ au} = 20 \text{ cm}^{-1}.
\]

The main point to be noted is that the condition (16) is established whatever the degree of excitation of the Rydberg atom may be. This should explain the failure of the binary encounter theory (which is based upon similar although more restrictive conditions) to predict inelastic collision cross sections (Gounand et al 1977).

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**References**


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\(^\dagger\) This result can also be established from wave mechanics (Omont 1977, equations (3)–(15)).
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