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# Multistate Impact-Parameter Calculation of Atom-Atom Excitation Cross Sections: Excitation of Atomic Hydrogen by Neon, Argon, and Krypton†

Hiram Levy II

*Smithsonian Astrophysical Observatory, Cambridge, Massachusetts* 02138

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Excitation cross sections for the collisions H(1*s*) + Ne, Ar, Kr → H(2*s*, 2$p_0$, 2$p_\pm$) + Ne, Ar, Kr are calculated over the velocity range of 0.3–5.0 a.u. in the distorted Born, two-state (for argon only), and four-state impact-parameter approximations that do not allow for electron exchanges between the colliding atoms. The results are compared with earlier first Born and scaled first Born calculations and with experimental data. The four-state cross sections, while greatly reduced from the first Born results, are still between three and ten times greater than experiment. Polarization fractions are also calculated from the four-state cross sections and compared with experimental data and with previous calculations.

## I. INTRODUCTION

In a recent paper, to be referred to as I, Levy[1] presented a general method for evaluating the time-dependent matrix elements occurring in multistate impact-parameter calculations of atom-atom inelastic collisions. The method does not allow for electron exchanges between projectile and target atoms, but it does permit the inclusion of all the direct couplings.

First Born wave calculations[2] of excitation and ionization cross sections for H(1*s*) in collision with rare gases in their ground states gave values for the heavier target atoms that are many times larger than the experimental values, even at high incident velocities. However, the substitution of a velocity-dependent scaling factor $\eta_B(v_1)$ [determined by fitting theoretical ionization cross-section calculations to experimental results] for $Z_B$, the nuclear charge of the target atom $B$ in the cross-section equations resulted in good agreement between theoretical and experimental excitation cross sections for neon, argon, and krypton targets.

While the use of velocity-dependent scaling factors was successful in this instance, it was not possible to isolate the physical effects most responsible for the large deviation of the first Born wave calculations from experiment.

In this paper, the effects of distortion, coupling to the initial state, and couplings among the final excited states (2$p_0$, 2$p_+$, 2$p_-$, and 2*s*) are considered in order to determine their importance as corrections to the first Born wave treatment.

## II. THEORY

The general formulation of multistate impact-parameter calculations and, in particular, the means of evaluating the required time-dependent matrix elements have been presented in I and will not be discussed here in great detail.

We wish to solve the truncated set of coupled differential equations:

$$i\dot{a}_n(t) = \sum_{m=1}^{N} a_m(t) V_{nm}[\vec{R}(t)](e^{itE_{nm}}), \quad n = 1 \to N, \tag{1}$$

where $E_{nm} = E_n - E_m$ is the transition energy, (2)

and

$$V_{nm}[\vec{R}(t)] = \int d\vec{r}_A \int d\vec{r}_B \, \phi_i^{A*} \phi_u^{B*} \times V[\vec{r}_A, \vec{r}_B, \vec{R}(t)] \phi_j^A \phi_v^B \tag{3}$$

is the electrostatic interaction between the projectile atom $A$ and the target atom $B$ integrated over the $n$th and $m$th electronic scattering states, which are themselves products of the atomic wave functions $\phi_i{}^A$ and $\phi_u{}^B$.

The probability of a transition from the initial state to a final state $n$,

$$P_n{}^N(\rho) = |a_n(+\infty)|^2 \quad , \tag{4}$$

is then integrated over the impact parameter for a particular incident velocity $v_i$ to give the $N$-state cross section

$$Q^N(n) = 2\pi \int_0^\infty \rho d\rho \, P_n{}^N(\rho) \quad . \tag{5}$$

In the calculations, five states, $(1s)(N^1S)$, $(2p_0)(N^1S)$, $(2p_+)(N^1S)$, $(2p_-)(N^1S)$, and $(2s)(N^1S)$, where $(N^1S)$ represents the ground state of a particular rare gas and $(nl)$ is an atomic state of hydrogen, are included in Eq. (1). An appropriate choice of phase factors[3] reduces the five coupled equations to four.

The necessary time-dependent matrix elements $V_{nm}[\vec{R}(t)]$ are found by substituting $Z_B$($B$ = Ne, Ar, Kr) or if one desires velocity-dependent scaled potentials $\eta_B(v_i)$ for $Z_{He}$ in Eq. (10) of I.

The scalar quantities $V_{nm}{}^L(R)$ and $v_{nm}{}^L(R)$ occurring in Eq. (10) of I were calculated by use of the rare-gas elastic x-ray form factors of Cromer and Mann,[4] the generalized Born matrix elements for hydrogen discussed in I, and a single numerical Simpson's rule integration. They are available, upon request, from the author.

The multistate calculations apply to collisions in which the target atom is not excited. For comparison with experimental total excitation cross sections, we use

$$\sigma^4(nl) = Q^4(nl) + \sigma_I(nl) \quad , \tag{6}$$

where $\sigma_I(nl)$, calculated by use of the closure approximation,[2] is the first Born wave cross section for excitation of the projectile to state $nl$ and the target to any state other than its ground state. As in I, all subscript references to the target atom are dropped and atomic units are used throughout.

## III. RESULTS AND DISCUSSION

Excitation cross sections for the collisions H($1s$) + Ne → H($2s$, $2p_0$, $2p_\pm$) + Ne have been calculated to a computational uncertainty of 1.0% in the distorted Born approximation ($\sigma_{DB}$) and in the four-state impact-parameter ($Q^4$) approximations and are listed together with first Born wave calculations[2] in Table I. As was found for a helium target in I, distortion effects provide the major correction to the first

TABLE I. Cross sections for H($1s$) + Ne → H($2s$, $2p_0$, $2p_\pm$) + Ne.

| $v_i$ a.u. | $Q^4(2s)$ ($a_0^2$) | $\sigma_{DB}(2s)$ ($a_0^2$) | $\sigma_B(2s)$ [a] ($a_0^2$) | $Q^4(2p_0)$ ($a_0^2$) | $\sigma_{DB}(2p_0)$ ($a_0^2$) | $Q^4(2p_\pm)$ ($a_0^2$) | $\sigma_{DB}(2p_\pm)$ ($a_0^2$) | $\sigma_B(2p)$ [a] ($a_0^2$) |
|---|---|---|---|---|---|---|---|---|
| 5.0 | $6.06^{-2}$ [b] | | $6.16^{-2}$ | $5.56^{-3}$ | | $5.90^{-2}$ | | $1.21^{-1}$ |
| 3.0 | $1.63^{-1}$ | | $1.71^{-2}$ | $3.95^{-2}$ | | $1.55^{-1}$ | | $3.35^{-1}$ |
| 2.0 | $3.43^{-1}$ | $3.43^{-1}$ | $3.85^{-1}$ | $1.71^{-1}$ | $1.68^{-1}$ | $3.16^{-1}$ | $3.25^{-1}$ | $7.53^{-1}$ |
| 1.4 | $6.10^{-1}$ | | $7.86^{-1}$ | $5.33^{-1}$ | | $5.35^{-1}$ | | 1.52 |
| 1.0 | $8.97^{-1}$ | $9.20^{-1}$ | 1.54 | 1.22 | 1.27 | $7.55^{-1}$ | $8.40^{-1}$ | 2.90 |
| 0.8 | $9.94^{-1}$ | | 2.38 | 1.72 | | $8.35^{-1}$ | | 4.31 |
| 0.6 | $9.46^{-1}$ | $8.83^{-1}$ | 4.13 | 2.10 | 2.09 | $7.65^{-1}$ | $9.57^{-1}$ | 6.66 |
| 0.5 | $9.24^{-1}$ | | 5.59 | 2.12 | | $6.15^{-1}$ | | 8.11 |
| 0.4 | $8.31^{-1}$ | | 7.58 | 1.71 | | $3.72^{-1}$ | | 9.04 |
| 0.3 | $4.87^{-1}$ | $2.12^{-1}$ | 9.06 | $7.94^{-1}$ | $6.79^{-1}$ | 1.20 | $1.94^{-1}$ | 7.65 |

[a] These data are from a previous calculation, (Ref. 2).
[b] The exponent gives the power of 10 by which the entry must be multiplied.

Born. Couplings both to the initial state and among the final excited states are more important at low velocities for a neon target than they are for helium.

An unusual result is the peaking of $Q^4(2s)$ at $v_i = 0.8$ a.u., which is a considerably higher velocity than that observed for the other targets studied. This is apparently due to the nonlinear dependence of the cross sections on the size of the interaction matrix elements. Thus, for neon, the effects of coupling between the $2p$ and $2s$ final states are quite small relative to distortion, and the maximum of $Q^4(2s)$ is determined solely by the effects of distortion.

The same excitation cross sections are calculated with a computational uncertainty of 1.0% for an argon target atom in the distorted Born, two-state impact-parameter ($Q^2$) and four-state impact-parameter approximations, and, together with first Born wave calculations,[2] are listed in Table II.

Again the major correction is distortion, though the other couplings are now important for $v_i \leq 2.0$ a.u. As was observed in I for helium, coupling to the initial state reduces all the cross sections at all incident velocities considered. The $2s$ and $2p_0$ cross sections are increased at all energies considered by couplings between the final excited states, while the $2p_\pm$ cross section is increased only at low energies and decreased otherwise.

The same excitation cross-section calculations for a krypton target atom are listed together with first Born wave results[2] in Table III.

Of those considered, the major correction to the first Born wave approximation for all three target atoms results from distortion effects. The size of

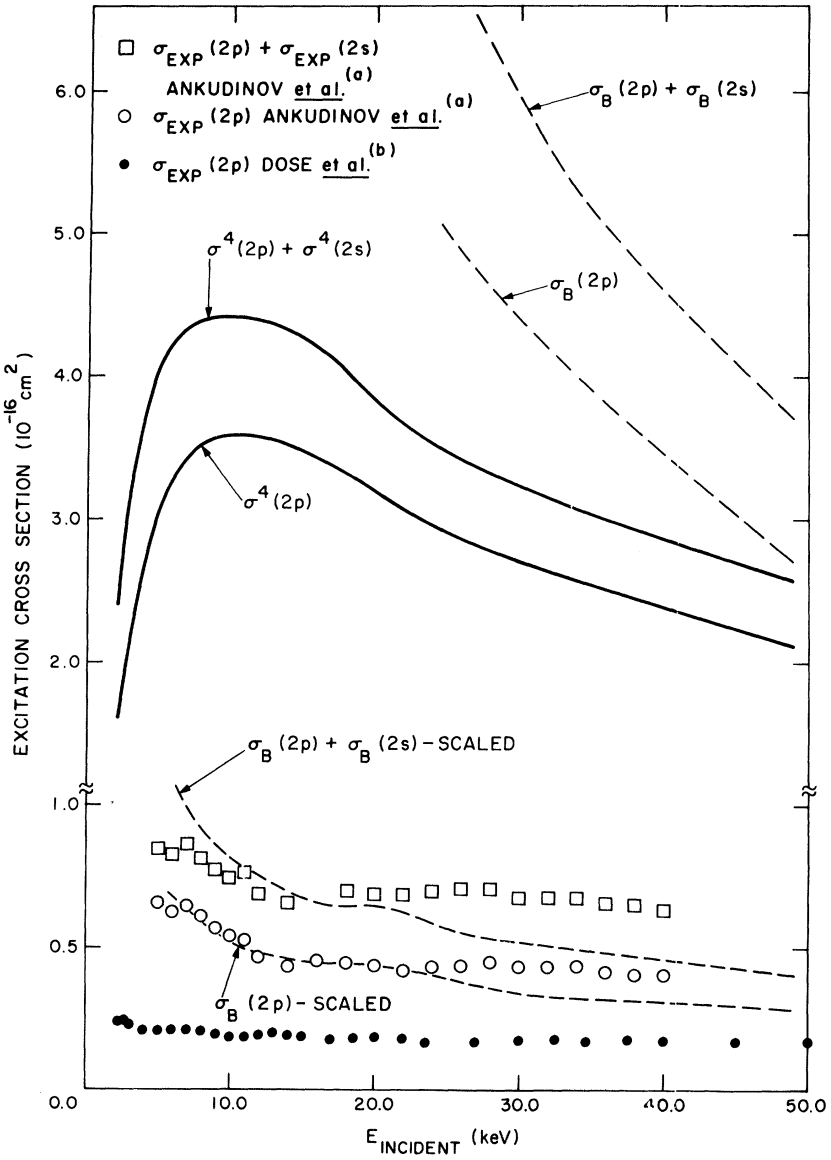


FIG. 1. Excitation cross sections for $H(1s) + Ar \rightarrow H(2s, 2p_0, 2p_\pm) + Ar$. (a) see Refs. 6 and 7, (b) see Ref. 5.

TABLE II. Cross sections for $H(1s) + Ar \rightarrow H(2s, 2p_0, 2p_\pm) + Ar$.

| $v_i$ a.u. | $Q^4(2s)$ $(a_0^2)$ | $Q^2(2s)$ $(a_0^2)$ | $\sigma_{DB}(2s)$ $(a_0^2)$ | $\sigma_B(2s)$ [a] $(a_0^2)$ | $Q^4(2p_0)$ $(a_0^2)$ | $Q^2(2p_0)$ $(a_0^2)$ | $\sigma_{DB}(2p_0)$ $(a_0^2)$ | $Q^4(2p_\pm)$ $(a_0^2)$ | $Q^2(2p_\pm)$ $(a_0^2)$ | $\sigma_{DB}(2p_\pm)$ $(a_0^2)$ | $\sigma_B(2p)$ [a] $(a_0^2)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5.0 | $3.12^{-1}$ [b] | | | $3.34^{-1}$ | $8.67^{-2}$ | | | $3.52^{-1}$ | | | $7.61^{-1}$ |
| 3.0 | $7.57^{-1}$ | | | $9.29^{-1}$ | $5.21^{-1}$ | | | $8.50^{-1}$ | | | 2.11 |
| 2.0 | 1.29 | 1.12 | 1.31 | 2.09 | 1.66 | 1.65 | 1.81 | 1.50 | 1.68 | 1.73 | 4.74 |
| 1.4 | 1.62 | | | 4.26 | 3.33 | | | 2.12 | | | 9.58 |
| 1.0 | 1.97 | 1.27 | 1.50 | 8.32 | 5.45 | 4.46 | 5.36 | 2.49 | 3.20 | 3.52 | $1.81^{+1}$ |
| 0.8 | 2.46 | | | $1.29^{+1}$ | 7.20 | | | 2.48 | | | $2.67^{+1}$ |
| 0.6 | 2.98 | 1.16 | 1.27 | $2.19^{+1}$ | 8.58 | 5.72 | 7.30 | 2.09 | 2.97 | 3.56 | $4.00^{+1}$ |
| 0.5 | 3.31 | | | | 8.56 | | | 1.68 | | | $4.71^{+1}$ |
| 0.4 | 3.43 | | | $3.81^{+1}$ | 7.33 | | | 1.15 | | | $4.95^{+1}$ |
| 0.3 | 2.81 | $3.45^{-1}$ | $3.45^{-1}$ | $4.12^{+1}$ | 4.50 | 2.07 | 3.55 | $6.20^{-1}$ | $5.52^{-1}$ | $7.55^{-1}$ | $3.71^{+1}$ |

[a] These data are from a previous calculation (Ref. 2).
[b] The exponent gives the power of 10 by which the entry must be multiplied.

TABLE III. Cross sections for $H(1s) + Kr \rightarrow H(2s, 2p_0, 2p_\pm) + Kr$.

| $v_i$ a.u. | $Q^4(2s)$ $(a_0^2)$ | $\sigma_{DB}(2s)$ $(a_0^2)$ | $\sigma_B(2s)$ $(a_0^2)$ | $Q^4(2p_0)$ $(a_0^2)$ | $\sigma_{DB}(2p_0)$ $(a_0^2)$ | $Q^4(2p_\pm)$ $(a_0^2)$ | $\sigma_{DB}(2p_\pm)$ $(a_0^2)$ | $\sigma_B(2p)$ [a] $(a_0^2)$ |
|---|---|---|---|---|---|---|---|---|
| 5.0 | $6.31^{-1}$ [b] | | $7.41^{-1}$ | $3.03^{-1}$ | | $7.35^{-1}$ | | 1.71 |
| 3.0 | 1.30 | | 2.06 | 1.46 | | 1.63 | | 4.74 |
| 2.0 | 1.75 | 1.80 | 4.63 | 3.43 | 3.99 | 2.58 | 3.35 | $1.06^{+1}$ |
| 1.4 | 2.29 | | 9.45 | 6.23 | | 3.34 | | $2.14^{+1}$ |
| 1.0 | 3.23 | 2.02 | $1.84^{+1}$ | $1.01^{+1}$ | $1.02^{+1}$ | 3.64 | 6.54 | $4.05^{+1}$ |
| 0.8 | 4.19 | | $2.85^{+1}$ | $1.29^{+1}$ | | 3.99 | | $5.94^{+1}$ |
| 0.6 | 5.72 | 1.72 | $4.84^{+1}$ | $1.54^{+1}$ | $1.35^{+1}$ | 2.95 | 6.85 | $8.87^{+1}$ |
| 0.5 | 6.77 | | $6.47^{+1}$ | $1.57^{+1}$ | | 2.55 | | $1.04^{+2}$ |
| 0.4 | 7.80 | | $8.39^{+1}$ | $1.42^{+1}$ | | 2.17 | | $1.09^{+2}$ |
| 0.3 | 7.65 | 5.09 | $9.08^{+1}$ | $1.03^{+1}$ | 9.52 | 1.93 | 1.85 | $8.09^{+1}$ |

[a] These data are from a previous calculation (Ref. 2).
[b] The exponent gives the power of 10 by which the entry must be multiplied.

TABLE IV. Polarization fractions.

| $v_i$ (a.u.) | $P_4^{Ne}$ (2p) | $P_4^{Ar}$ (2p) | $P_4^{Kr}$ (2p) |
|---|---|---|---|
| 5.0 | −23.7 | −17.8 | −12.7 |
| 3.0 | −17.5 | −7.6 | −1.8 |
| 2.0 | −9.3 | +1.7 | +4.9 |
| 1.4 | −0.1 | +7.8 | +10.8 |
| 1.0 | +8.3 | +13.5 | +17.5 |
| 0.8 | +12.5 | +18.2 | +19.9 |
| 0.6 | +17.3 | +23.4 | +26.6 |
| 0.5 | +20.9 | +26.3 | +28.6 |
| 0.4 | +25.0 | +29.0 | +29.3 |
| 0.3 | +29.4 | +30.4 | +26.9 |

all the corrections and maximum incident velocity at which they become important increase with increasing target nuclear charge as do the matrix elements themselves.

In Fig. 1, the first Born, the scaled first Born, and the four-state impact-parameter results are compared with the experimental data of Dose, Gunz, and Meyer[5] and of Ankudinov, Andreev, Orbeli, and Dukelskii[6] for an argon target atom where the values of $\sigma_1$ were taken from previous calculations.[2]

At low energies, the four-state cross sections, while greatly reduced from the first Born values, are still 5–7 times greater than experiment. At 50.0 keV, they are approaching the first Born values, which remain five times larger than experiment. Neglect of electron exchanges between the two atoms may cause the discrepancy at low velocity, but it seems to be a less plausible explanation of the discrepancy at high velocities. The results for neon and krypton target atoms show similar behavior over the energy range studied.

Thus, while distortion and couplings to the initial state and among final states make important corrections to the first Born calculations, serious disagreement still exists between theory and experiment for collisions of hydrogen atoms with heavy target atoms. Until specific further corrections can be determined, in particular the inclusion of electron exchanges between the atoms, it appears that a scaled Born calculation is the simplest and most accurate procedure for predicting cross sections.

The polarization fractions for the $2p_m$ excitations, $P_N(2p)$, calculated from the four-state cross sections by use of the formula of Percival and Seaton,[7]

$$P_N(2p) = 300\left(\frac{Q^N(2p_0) - Q^N(2p_\pm)}{7Q^N(2p_0) + 11Q^N(2p_\pm)}\right), \qquad (7)$$

are presented in Table IV.

The values calculated from the exact-state cross sections agree well at low energies with the theoretical results of Dose,[8] which do not include coupling to the initial state or coupling between the 2s and 2p final states. However, his results drop off much more rapidly with increasing velocity than do the complete four-state calculations.

The four-state results do not agree well with the experimental results of Dose *et al.*[9] in magnitude for neon though the slopes are similar, but there is good agreement between theory and experiment for argon at $v_i > 0.6$ a. u.

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