

Coupled-state calculations of proton-hydrogen-atom scattering with a Sturmian expansion*

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Cross sections for proton-hydrogen-atom scattering have been calculated for protons incident in the energy range 15–200 keV. The impact-parameter Schrödinger equation was solved approximately with an expansion in Sturmian functions; the expansion contained a total of six s -state and six p -state functions centered about each proton. Results are presented and discussed for excitation to the $n = 2$ level, for charge transfer to the ground state and the $n = 2$ level, and for ionization.

I. INTRODUCTION

One of the most fundamental scattering systems encountered in the study of ion-atom collisions is the proton-hydrogen-atom system. Provided that the incident energy is above a few hundred electron volts, the full three-body problem can be reduced to the problem of an electron moving in a time-dependent field, since the two protons are heavy and can be treated as distinguishable classical particles which move with constant velocity.¹ Despite this enormous simplification, usually referred to as the impact-parameter approximation, the resulting equation for the electron wave function has not been solved exactly, and cross sections for nonresonant transitions have not yet been calculated to satisfactory accuracy in the energy range below 200 keV. The purpose of this paper is to report an attempt to obtain improved estimates of the cross sections for excitation and charge transfer to the $n = 2$ level of hydrogen atoms by protons incident in the energy range 15–200 keV.

To some extent the present approach follows that of Gallaher and Wilets.² The impact-parameter Schrödinger equation

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = H(t) |\Psi(t)\rangle \quad (1.1)$$

for the state vector $|\Psi(t)\rangle$ of the electron is solved approximately with a trial solution $|\Psi_{\text{tr}}(t)\rangle$ which is a linear combination of Sturmian basis vectors with time-dependent coefficients that satisfy the standard coupled-state equations, i.e., Eqs. (1.4) below. (In the calculations reported here six s -state and six p -state basis functions were centered about each proton.) A Sturmian expansion has the particular merit that the Sturmian functions form a discrete set which, in its entirety, is complete. Therefore estimates of transition probabilities calculated with a Sturmian expansion become exact as the basis set is enlarged. This is in contrast to the case where an expansion in terms of bound atomic orbitals is used; although estimates of transition

probabilities calculated with an atomic orbital expansion converge as the (discrete) basis set is enlarged, the values to which they converge are incorrect, a point sometimes overlooked in the literature. Another merit of the Sturmian expansion is that the Sturmian functions satisfy a recurrence relation which greatly facilitates the evaluation of the required matrix elements.³ However, the use of a Sturmian expansion has the following consequence: The natural expression to take for the estimate of the probability that after the collision is over the electron is bound to proton α in the state k is

$$\lim_{t \rightarrow \infty} |\langle \Phi_{k\alpha}(t) | \Psi_{\text{tr}}(t) \rangle|^2,$$

where $|\Phi_{k\alpha}(t)\rangle$ represents the state $k\alpha$. It turns out, however, that if the radial wave function representing the state $k\alpha$ has nodes, this limit does not exist; rather, $|\langle \Phi_{k\alpha}(t) | \Psi_{\text{tr}}(t) \rangle|^2$ tends to a constant term *plus* a term which oscillates without limit as $t \rightarrow \infty$. The nonexistence of the above limit is due to the fact that the state $k\alpha$ cannot be represented exactly by a *finite* linear combination of Sturmian functions. However, provided that the basis set is sufficiently large, one can find a suitable approximate representation $|\Phi_{k\alpha, \text{tr}}(t)\rangle$ of the state $k\alpha$ such that the quantity

$$P_{k\alpha, \text{tr}} = \lim_{t \rightarrow \infty} |\langle \Phi_{k\alpha, \text{tr}}(t) | \Psi_{\text{tr}}(t) \rangle|^2 \quad (1.2)$$

is a well-defined variational estimate of the probability for the electron to undergo a transition to the state $k\alpha$.³ The vector $|\Phi_{k\alpha, \text{tr}}(t)\rangle$ is chosen as follows: Let $H_{\alpha}(t)$ denote the Hamiltonian of the hydrogen atom whose nucleus is α . (The Hamiltonian $H_{\alpha}(t)$ is time dependent only because we use a coordinate system whose origin is at the midpoint of the two protons.) Assume that K basis functions are centered about each proton. If a K -dimensional matrix representation of $H_{\alpha}(t)$ is formed from K orthonormal linear combinations of those Sturmian basis functions centered about α , the eigenvalues of this matrix yield variational

estimates of (and upper bounds on) the binding energies of the first few states of the hydrogen atom. The vector $|\Phi_{k\alpha, \text{tr}}(t)\rangle$ is chosen to be the eigenvector whose eigenvalue is a variational estimate of the binding energy of the state $k\alpha$; the limit of $|\langle \Phi_{k\alpha, \text{tr}}(t) | \Psi_{\text{tr}}(t) \rangle|^2$, as $t \rightarrow \infty$, is then well defined and is a variational estimate of the transition probability. This is the expression which was used to estimate transition probabilities in the calculation reported on here.

The trial state vector for the electron can be expressed in the form

$$|\Psi_{\text{tr}}(t)\rangle = \sum_{\pi=\pm} \sum_{k=1}^K \mathcal{G}_k^\pi(t) |\Phi_{k, \text{tr}}^\pi(t)\rangle, \quad (1.3)$$

where

$$|\Phi_{k, \text{tr}}^\pi(t)\rangle = (1/\sqrt{2})(1 + \pi P) |\Phi_{k\alpha, \text{tr}}(t)\rangle,$$

where α denotes either the target proton or the incident proton, and where P is the operator which reflects the coordinates of the electron through the midpoint of the two protons. The eigenvalues of P are $\pi = \pm 1$. The time-dependent coefficients $\mathcal{G}_k^\pi(t)$ are specified at time $t = -\infty$ and they satisfy the standard coupled-state equations, namely,

$$i\hbar \frac{d}{dt} \vec{\mathcal{A}}^\pi(t) = \underline{G}^\pi(t) \vec{\mathcal{A}}^\pi(t), \quad \pi = \pm, \quad (1.4)$$

where $\vec{\mathcal{A}}^\pi(t)$ is a column vector whose elements are the coefficients $\mathcal{G}_k^\pi(t)$ and where

$$\underline{G}^\pi(t) = [\underline{N}^\pi(t)]^{-1} \underline{M}^\pi(t),$$

$$[\underline{N}^\pi(t)]_{jk} = \langle \Phi_{j, \text{tr}}^\pi(t) | \Phi_{k, \text{tr}}^\pi(t) \rangle, \quad (1.5)$$

$$[\underline{M}^\pi(t)]_{jk} = \langle \Phi_{j, \text{tr}}^\pi(t) | H(t) - i\hbar \frac{d}{dt} | \Phi_{k, \text{tr}}^\pi(t) \rangle.$$

Equations (1.4) would normally be integrated from some large negative time to some large positive time. However, $\underline{G}^\pi(t)$ need be evaluated only at negative times, since it follows from the invariance of the Hamiltonian $H(t)$ under time reversal that^{4,5}

$$\underline{G}^\pi(t) = \underline{D} \underline{G}^\pi(-t) \underline{D}^*, \quad (1.6)$$

where \underline{D} is a time-independent unitary diagonal matrix defined in Ref. 5. Usually^{6,7} $\underline{G}^\pi(t)$ is stored on a mesh of points at negative times. However, as the basis set is enlarged the storage requirements soon become excessive. In the calculation reported on here, the need to store $\underline{G}^\pi(t)$ was avoided by the following method: Rather than integrate Eqs. (1.4) for the vectors $\vec{\mathcal{A}}^\pi(t)$, one finds the matrices $\underline{O}^\pi(t)$ which govern the time-dependence of these vectors. With $\vec{\mathcal{A}}^\pi(t)$ specified at some large negative time $-T$, the formal solutions of Eqs. (1.4) are

$$\vec{\mathcal{A}}^\pi(t) = \underline{O}^\pi(t, -T) \vec{\mathcal{A}}^\pi(-T), \quad \pi = \pm, \quad (1.7)$$

where

$$i\hbar \frac{d}{dt} \underline{O}^\pi(t, -T) = \underline{G}^\pi(t) \underline{O}^\pi(t, -T), \quad (1.8)$$

$$\underline{O}^\pi(-T, -T) = \underline{I}, \quad \pi = \pm,$$

where \underline{I} denotes the identity matrix.

As a consequence of Eq. (1.6) the matrices $\underline{O}^\pi(t, -T)$ have the property^{3,8}

$$\underline{O}^\pi(T, -T) = [\underline{N}^\pi(T)]^{-1} \underline{D} \tilde{\underline{O}}^\pi(0, -T) \underline{D}^* \underline{N}^\pi(0) \underline{O}^\pi(0, -T), \quad (1.9)$$

where the tilde denotes the transpose of $\underline{O}^\pi(0, -T)$. Noting that for T sufficiently large $\underline{N}^\pi(T)$ is the identity matrix, it follows from Eqs. (1.7) and (1.9) that

$$\vec{\mathcal{A}}^\pi(T) = \underline{D} \tilde{\underline{O}}^\pi(0, -T) \underline{D}^* \underline{N}^\pi(0) \vec{\mathcal{A}}^\pi(0). \quad (1.10)$$

Therefore to find $\vec{\mathcal{A}}^\pi(t)$ at the large positive time $t = T$, Eqs. (1.8) need be integrated only from $t = -T$ to $t = 0$, and $\underline{G}^\pi(t)$ need be evaluated only at negative times. No storage of $\underline{G}^\pi(t)$ is necessary.

Since the Sturmian functions form a complete set, they overlap the continuum eigenfunctions of the hydrogen atom. As a result, the coefficients of the basis vectors contain information about the probability for ionization. The procedure for extracting this information is discussed in Sec. II of this paper. In Sec. III the results are presented and discussed. In the Appendix the numerical methods of the calculation are briefly described.

II. IONIZATION PROBABILITY

To obtain a simple estimate of the ionization probability, we estimate the probability for a transition to each bound state, add these probabilities, and subtract from unity. The result is an estimate of the ionization probability which does not require a knowledge of the asymptotic form of the wave function for the ionized electron.

We cannot estimate the probability for a transition to a highly excited state from Eq. (1.2), since only the first few states of the hydrogen atom can be represented by the trial vectors $|\Phi_{k\alpha, \text{tr}}(t)\rangle$, and even fewer can be represented well. We therefore proceed as follows: The exact expression for the probability of a transition to the state $k\alpha$ is

$$P_{k\alpha} = \lim_{t \rightarrow \infty} |\langle \Phi_{k\alpha}(t) | \Psi(t) \rangle|^2. \quad (2.1)$$

Equation (2.1) is exactly equivalent to

$$P_{k\alpha} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_t^{2t} dt' |\langle \Phi_{k\alpha}(t') | \Psi(t') \rangle|^2. \quad (2.2)$$

In analogy with Eq. (2.2), an approximate expression for the transition probability is

$$P'_{k\alpha, \text{tr}} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_t^{2t} dt' |\langle \Phi_{k\alpha}(t') | \Psi_{\text{tr}}(t') \rangle|^2, \quad (2.3)$$

provided that the limit exists. We now show that the limit does exist. Assume, for simplicity only, that the time-dependent phase of each basis vector $|\Phi_{k\alpha, \text{tr}}(t)\rangle$ is chosen to be $e^{-iE_{k, \text{tr}}t/\hbar}$, where $E_{k, \text{tr}}$ is the variational estimate of the binding energy of the electron in state $k\alpha$. Then it is not difficult to see that the coefficients $\mathcal{G}_n^\pi(t)$ appearing in the expansion of Eq. (1.3) have well-defined limits as $t \rightarrow \infty$. Denoting these limits by b_k^π , and noting that $|\langle \Phi_{k\alpha}(t) | \Phi_{j\alpha, \text{tr}}(t) \rangle|$ is time independent and that $\langle \Phi_{k\alpha}(t) | P | \Phi_{j\alpha, \text{tr}}(t) \rangle$ is zero in the limit $t \rightarrow \infty$, Eq. (2.3) becomes, on replacing $|\Psi_{\text{tr}}(t')\rangle$ by the expansion of Eq. (1.3),

$$\begin{aligned} P'_{k\alpha, \text{tr}} &= \frac{1}{2} \sum_{j=1}^K |(b_j^+ \pm b_j^-) \langle \Phi_{k\alpha} | \Phi_{j\alpha, \text{tr}} \rangle|^2 \\ &\quad + \frac{1}{2} \sum_{\substack{i, j=1 \\ i \neq j}}^K \beta_{ij} (b_i^+ \pm b_i^-) (b_j^+ \pm b_j^-)^* \\ &\quad \times |\langle \Phi_{k\alpha} | \Phi_{i\alpha, \text{tr}} \rangle \langle \Phi_{k\alpha} | \Phi_{j\alpha, \text{tr}} \rangle|, \end{aligned} \quad (2.4)$$

where

$$\beta_{ij} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_t^{2t} dt' e^{-i(E_{i, \text{tr}} - E_{j, \text{tr}})t'/\hbar},$$

and where the choice of the sign in the right-hand side of Eq. (2.4) is determined by α . We suppress the argument t in terms which are independent of t . If the states $i\alpha$ and $j\alpha$ have different symmetry, at least one of these states must have a symmetry different from $k\alpha$, and it follows that in this case $\langle \Phi_{k\alpha} | \Phi_{i\alpha, \text{tr}} \rangle \langle \Phi_{k\alpha} | \Phi_{j\alpha, \text{tr}} \rangle$ is zero. If the states $i\alpha$ and $j\alpha$ have the same symmetry but $i \neq j$, then $E_{i, \text{tr}} \neq E_{j, \text{tr}}$ and it follows that in this case β_{ij} is zero. The second term on the right-hand side of Eq. (2.4) is therefore zero, and Eq. (2.4) reduces to

$$P'_{k\alpha, \text{tr}} = \frac{1}{2} \sum_{j=1}^K |(b_j^+ \pm b_j^-) \langle \Phi_{k\alpha} | \Phi_{j\alpha, \text{tr}} \rangle|^2. \quad (2.5)$$

We pause here to remark on the difference between $P_{k\alpha, \text{tr}}$ and $P'_{k\alpha, \text{tr}}$. We first note that $P'_{k\alpha, \text{tr}}$ is the expression calculated by Gallaher and Willets.² Now in terms of b_j^π , Eq. (1.2) becomes

$$P_{k\alpha, \text{tr}} = \frac{1}{2} |b_k^+ \pm b_k^-|^2. \quad (2.6)$$

We have already noted that $P_{k\alpha, \text{tr}}$ is a *variational* estimate of the transition probability, that is, an estimate which is accurate to second order in the error in $|\Psi_{\text{tr}}(t)\rangle$. Evidently $P_{k\alpha, \text{tr}}$ and $P'_{k\alpha, \text{tr}}$ become identical as the basis set is enlarged. The difference between $P_{k\alpha, \text{tr}}$ and $P'_{k\alpha, \text{tr}}$ is, in fact, second order, since $|\langle \Phi_{k\alpha} | \Phi_{j\alpha, \text{tr}} \rangle|$ is equal to δ_{kj} to second

order in the difference between $\Phi_{k\alpha}$ and $\Phi_{k\alpha, \text{tr}}$.³ It follows that $P'_{k\alpha, \text{tr}}$ is a variational estimate of the transition probability whenever $P_{k\alpha, \text{tr}}$ is, that is, whenever the basis set is sufficiently large that $\Phi_{k\alpha, \text{tr}}$, and hence $P_{k\alpha, \text{tr}}$, can be defined.⁹ Therefore it is not obvious which of the two expressions $P_{k\alpha, \text{tr}}$ and $P'_{k\alpha, \text{tr}}$ provides the more accurate estimate of the transition probability.

Returning to the problem of determining the ionization probability, we sum Eq. (2.5) over all bound states to estimate the probability for the electron to be bound finally. We then subtract this probability from unity. If the two protons are denoted by A and B , so that α runs over A and B , we obtain for the estimate of the ionization probability

$$\begin{aligned} P_{\text{ion, tr}} &= 1 - \sum_{\substack{\text{all bound} \\ \text{states}}} P'_{k\alpha, \text{tr}} \\ &= 1 - \frac{1}{2} \sum_{\pi=\pm} \sum_{j=1}^K (1 - \Gamma_j) |b_j^+ + \pi b_j^-|^2, \end{aligned} \quad (2.7)$$

where, noting that owing to the identity of the protons A could just as well be replaced by B in the following:

$$\begin{aligned} \Gamma_j &= 1 - \sum_{\text{bound } k} |\langle \Phi_{kA} | \Phi_{jA, \text{tr}} \rangle|^2 \\ &= \int d^3q |\langle \vec{q}A | \Phi_{jA, \text{tr}} \rangle|^2, \end{aligned} \quad (2.8)$$

where $|\vec{q}A\rangle$ is a continuum eigenvector of the hydrogen atom whose nucleus is A . Using the unitarity condition

$$\sum_{\pi=\pm} \sum_{j=1}^K |b_j^+ + \pi b_j^-|^2 = 2, \quad (2.9)$$

Eq. (2.7) reduces to

$$P_{\text{ion, tr}} = \frac{1}{2} \sum_{\pi=\pm} \sum_{j=1}^K \Gamma_j |b_j^+ + \pi b_j^-|^2. \quad (2.10)$$

This expression has a simple interpretation; $\frac{1}{2} |b_j^+ + \pi b_j^-|^2$ is the probability for the electron to finally be in a state which has an overlap Γ_j with the continuum of the hydrogen atom.

We have not carried out an extensive convergence study of $P_{\text{ion, tr}}$. We have, however, studied the change in $P_{\text{ion, tr}}$ as the number of basis functions is changed in a trial wave function which includes only s states. The results are shown in Table I for the case when the impact energy is 25 keV and the impact parameter is 1 a.u. In this table N is the number of basis functions centered about each proton. It appears from the table that $P_{\text{ion, tr}}$ would converge to a value of about 0.14 if the entire set of s states were included; the convergence appears to be quite rapid, but of course it is not monotonic.

TABLE I. Estimate of the ionization probability as a function of the number N of basis states in a trial wave function containing s states only. The incident energy and impact parameter are 25 keV and 1 a.u., respectively.

N	$P_{\text{ion,tr}}$
2	0.161
3	0.117
4	0.121
5	0.139
6	0.139
7	0.138
8	0.135
9	0.139

III. RESULTS AND DISCUSSION

In the calculations reported on here 12 Sturmian functions were centered about each proton. Thus in accordance with the customary terminology we refer to these calculations as 12-state calculations. The functions included were the $1s$ to $6s$ and the $2p_{0,1}$ to $4p_{0,1}$. (Reflection symmetry in the scattering plane was exploited, so that p_1 refers to a linear combination of two states, one with magnetic quantum number equal to 1, the other -1 .) The target hydrogen atom was assumed to be initially in the ground state. The $2p$ states of the hydrogen atom were represented exactly, but the $2s$ state was represented only approximately; the degeneracy of the true $2s$ and $2p$ states was satisfied to within 0.6%. The beam axis was chosen to be the quantization axis.

In Fig. 1 we have plotted the cross section for excitation to the $n=2$ level versus the incident pro-

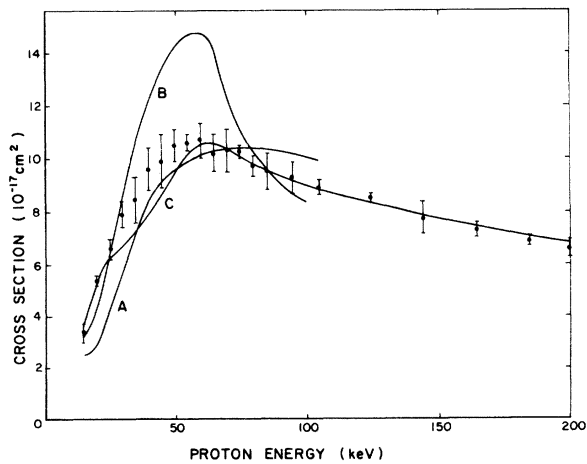


FIG. 1. Cross section for excitation to the $n=2$ level of the target hydrogen atom. A: four-state results of Cheshire *et al.* (Ref. 6); B: seven-state results of Cheshire *et al.* (Ref. 6); C: present results; \bullet : experimental results of Park *et al.* (Ref. 10).

ton energy (measured in the lab frame.) We have plotted the present results and the results obtained from four- and seven-state calculations by Cheshire *et al.*⁶ In the four-state calculations the $1s$, $2s$, and $2p_{0,1}$ states were coupled; in the seven-state calculations $3s$ and $3p_{0,1}$ pseudostates were also included. We have also plotted in Fig. 1 the recent experimental results of Park *et al.*¹⁰ The agreement between the present results and the experimental results is fairly good. Note, however, that the present results indicate a slight shoulder between 25 and 50 keV which does not appear in the experimental data. The large disagreement between the seven-state results of Ref. 6 and the experimental results in the energy range 40–70 keV is perhaps surprising, especially in view of the much better agreement between the four-state results of Ref. 6 and experiment. A possible explanation of this discrepancy is the following: The ionization cross section peaks in the energy range 40–70 keV and is large there. Therefore if pseudostates are included the flux into these pseudostates can be expected to be large in this energy range. However, the flux into the pseudostates cannot leak away to infinity, that is, the electron cannot become truly ionized. Therefore some of the flux entering the pseudostates may well leak back into the bound states as the collision progresses, yielding spurious contributions to the cross sections for bound-state transitions. This is not as likely to occur in the present calculation, since the electron is more nearly able to escape because of the inclusion of basis functions that extend over greater distances than those representing the $3s$ and $3p_{0,1}$ pseudostates of Ref. 6.

According to the results shown in Fig. 1 the cross section for excitation to the $n=2$ level has a peak at an energy roughly equal to 60 keV. In Table II we have presented the results for charge transfer to the $1s$ state and for excitation and charge transfer to the $2s$, $2p_0$, and $2p_1$ states. Referring to this table we see that above 25 keV the main contribution to the cross section for excitation to the $n=2$ level comes from excitation to the $2p$ states, and the peak in this cross section is due to peaks at 60 keV in the cross sections for excitation to the $2p$ states. The peaks in the $2p$ excitation cross sections are presumably the peaks one expects from Massey's rule.¹¹ This rule states that if ΔE is the difference in the initial and final binding energies of the electron, the cross section for the transition maximizes at a velocity roughly equal to $a\Delta E/\hbar$, where a is the range of interaction (which is roughly of the order of twice the impact parameter at which the transition occurs with maximum probability.) The rule follows from the uncertainty principle, which states that one must

TABLE II. Estimates of the cross sections for excitation and charge transfer to the $1s$, $2s$, $2p_0$, and $2p_1$ states in units of 10^{-17} cm^2 . Rows a refer to excitation and rows b to charge transfer. The beam axis is the quantization axis.

Energy (keV)	Final state			
	$1s$	$2s$	$2p_0$	$2p_1$
15 a		0.970	1.32	1.59
b	57.5	3.41	1.25	1.92
20 a		1.89	1.84	1.64
b	41.7	4.21	0.956	1.25
25 a		2.22	1.98	2.04
b	30.2	4.22	0.709	0.836
35 a		1.74	2.01	3.49
b	16.0	3.08	0.452	0.422
40 a		1.43	2.31	4.16
b	11.8	2.47	0.364	0.311
45 a		1.28	2.77	4.62
b	8.85	1.94	0.288	0.233
55 a		1.49	3.70	4.95
b	5.18	1.18	0.175	0.132
60 a		1.67	3.91	4.93
b	4.04	0.920	0.137	0.0994
70 a		1.77	3.75	4.84
b	2.53	0.572	0.0831	0.0575
125 a		0.813	2.59	4.88
b	0.331	0.0675	0.00936	0.00555
200 a		0.553	1.95	4.26
b	0.0492	0.00916	0.00110	0.00053

wait a time $\Delta t \approx \hbar/\Delta E$ to observe a change ΔE in the energy of a system. The time Δt is the collision time, which is roughly a/v , where v is the incident velocity. The Massey rule predicts a peak in the $2p$ excitation cross section at 60 keV if one inserts the reasonable value $a = 4.1$ a.u. for the interaction range. One expects the interaction range for excitation to the $2s$ state to be less than that for excitation to the $2p$ states, since there is no long-range dipole interaction coupling the $2s$ state to the ground state. Thus one expects a peak in the $2s$ excitation cross section at an energy less than 60 keV. Referring to Table II we see that there is indeed a peak in the $2s$ excitation cross section at 25 keV, corresponding to an interaction range of 2.7 a.u. The peak in the $2s$ excitation cross section seen at 70 keV in Table II is probably due to the degenerate coupling to the $2p$ states, which is expected to be most significant for energies close to where the $2p$ excitation cross section maximizes. (The calculations of Ref. 6, which were performed down to 1 keV, indicate an additional peak below 10 keV in each of the $2s$ and $2p$ excitation cross sections. Between 1 and 10 keV the cross section for

charge transfer to the $1s$ state is extremely large, and the additional peaks in the excitation cross sections are possibly due to the electron first being captured by the incident proton and then being captured back again by the target proton. That there is sufficient time for this to happen is supported by the interpretation¹² of the oscillations in the 3° charge transfer measurements of Lockwood and Everhardt.¹³)

Note from Table I that as the incident energy increases above 70 keV, excitation to the $2p_1$ state dominates with increasing significance over excitation to the $2p_0$ and $2s$ states. This is consistent with the first Born approximation, which predicts that the cross section for excitation to the $2p_1$ state decreases as $(\ln E)/E$ with increasing energy E , whereas the cross sections for excitation to the $2p_0$ and $2s$ states decrease as $1/E$. The $\ln E$ factor reflects the fact (which follows from energy-momentum considerations) that as the energy increases, the momentum transferred to the electron in distant collisions becomes directed perpendicular to the beam axis, so that the atom is preferentially oriented in this direction. Distant collisions are significant for $2p$ excitation because of the long-range dipole coupling. Note that there is a slight peak in the $2p_1$ excitation cross section at about 125 keV. This peak probably reflects the increasing importance of distant collisions (for $2p_1$ excitation) as the incident energy increases.

In Fig. 2 we have plotted the cross section for charge transfer to the $2s$ state. Both the present results and the seven-state results of Ref. 6 are shown. Also shown are the experimental results of Bayfield.¹⁴ The experimental data include cascade contributions (which amount to 6% or so), so that the experimental results ought to lie above the theoretical results, but they do not. However, the agreement between theory and experiment is fairly

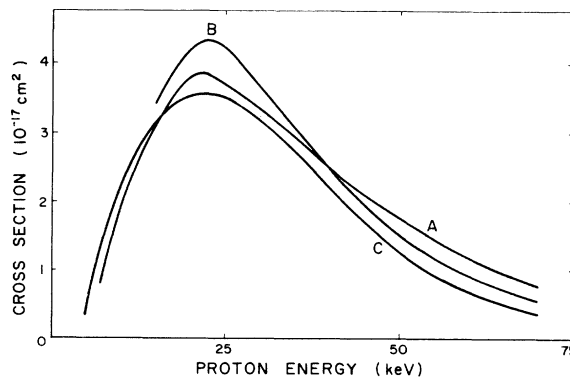


FIG. 2. Cross section for charge transfer to the $2s$ state. A: seven-state results of Cheshire *et al.* (Ref. 6); B: present results; C: experimental results of Bayfield (Ref. 14).

good. The cross section has a maximum between 20 and 25 keV. The Massey rule predicts such a maximum if the interaction range is taken to be roughly $a = 2.6$ a.u. However, the Massey rule should be applied with discretion to charge transfer, since other considerations can be more important; at high incident velocities the electron must acquire the velocity of the incident proton and the change in momentum of the electron becomes more important than the change in its binding energy.

The cross section for charge transfer to the 1s state is large at low energies, because the change in the binding energy of the electron is zero. However, this cross section decreases rapidly as the incident energy increases owing to the difficulty the electron has in acquiring the necessary momentum. The agreement between the present results and the seven-state results of Ref. 6 is particularly good at low incident energies, but the agreement worsens slightly with increasing energy. It is generally thought¹⁵ that at asymptotically high energies the second Born term provides the leading contribution to the cross section for charge transfer (in the forward direction). At high energies the second Born term corresponds to the classical picture¹⁶ in which the electron is scattered twice through 60° . The electron is first scattered with high speed towards the target proton; it is then scattered by the target proton and emerges from the collision with the velocity of the incident proton. According to this picture, the electron is intermediately scattered into a *continuum* state to which a large range of values of angular momentum *must* contribute (since the electron is scattered through a large angle into a small solid angle). Evidently, then, neither the present calculation nor the calculation of Ref. 6 can account for high-energy charge transfer, since a proper description of the intermediate scattering of the electron necessitates the inclusion of more than just the s and p components of the target continuum. That the difference between the charge transfer results of the present calculation and those of Ref. 6 becomes more noticeable at high energies is presumably because the former calculation includes more of the s and p subspace of the target continuum than does the latter.

In Fig. 3 we have plotted the ionization cross section computed according to the method outlined in Sec. II. These results are, over the entire energy range considered, roughly a factor of 2 smaller in magnitude than the recent experimental results of Park *et al.*¹⁷ However, the present results should not be taken too seriously, since they surely have not converged with respect to the inclusion of p states, which provide the major con-

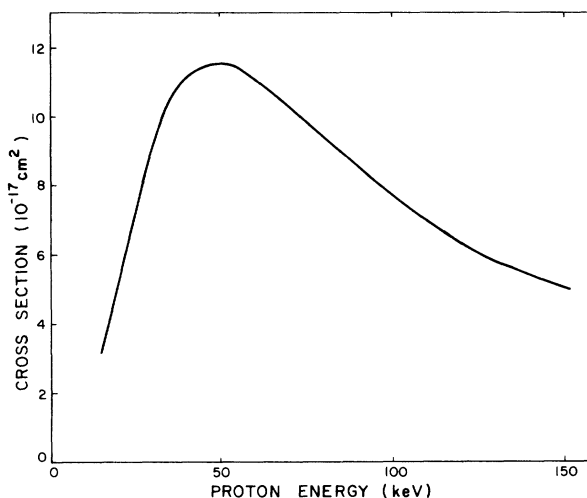


FIG. 3. Cross section for ionization (present results).

tribution to the cross section. We have included the present results for ionization because of the ease with which they were obtained once the coupled-state equations had been integrated. Although the method used can be expected to yield reliable results only if a large number of basis states are included, the method is, in principle, capable of yielding essentially exact results and it does account for charge transfer to the continuum, a mechanism not accounted for by the first Born and other simple approximations. It is interesting to note that the peak in the total ionization cross section seen in the present results occurs at roughly the same energy (about 55 keV) as found from experiment,¹⁷ whereas the peak found from the first Born approximation¹⁸ occurs at a lower energy (about 25 keV).

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APPENDIX A: NUMERICAL METHODS

In this appendix we use atomic units. The Hamiltonian of the electron can be expressed as

$$\begin{aligned} H(t) &= -\frac{1}{2}\nabla_{\vec{r}}^2 - 1/r_A - 1/r_B + f(\vec{R}) \\ &= H_A(t) - 1/r_B + f(\vec{R}) \\ &= H_B(t) - 1/r_A + f(\vec{R}), \end{aligned} \quad (\text{A1})$$

where $r_A = |\vec{r}_A|$ and $r_B = |\vec{r}_B|$, and where \vec{r}_A , \vec{r}_B , and \vec{r} , respectively, are the position vectors of the electron relative to the target proton A , to the incident proton B , and to the midpoint of A and B . The

position vector of B relative to A is $\vec{R} = \vec{b} + \vec{v}t$, where \vec{b} is the impact parameter and \vec{v} is the (constant) velocity of B relative to A . The choice of $f(\vec{R})$ is arbitrary; if an exact numerical integration of Eqs. (1.4) or (1.8) were to be performed, the resulting transition probabilities would be independent of the function $f(\vec{R})$.¹⁹ However, in practice this function effects the numerical accuracy of the calculated transition probabilities. In the calculations reported here $f(\vec{R})$ was chosen so as to reduce the oscillations in $O^\pi(t, -T)$. This was accomplished with the form

$$f(\vec{R}) = (1 - e^{-R})/R, \quad (\text{A2})$$

where $R = |\vec{R}|$. Two features of this form are noteworthy. First $f(\vec{R})$ is well behaved at $R = 0$, and second, $f(\vec{R})$ decreases as $1/R$ for large R .

The time-dependent phase factor of each basis vector $|\Phi_{k\alpha, \text{tr}}(t)\rangle$ was chosen to be $e^{-iE_{k, \text{tr}}t}$. For this choice of phase factors the equations

$$\langle \Phi_{k\alpha, \text{tr}}(t) | H_\alpha(t) - i \frac{d}{dt} | \Phi_{j\alpha, \text{tr}}(t) \rangle = 0, \quad j, k = 1, \dots, K, \quad (\text{A3})$$

are satisfied for all t . Therefore when the electron is localized about proton α the effective perturbation is determined by the matrix elements of $H(t) - H_\alpha(t)$. With $f(\vec{R})$ defined by Eq. (A2), this perturbation is bounded and it decreases as $1/R^2$ as $R \rightarrow \infty$; as a result, the phases of the elements of $O^\pi(t, -T)$ remain finite even in the limits $t \rightarrow \pm\infty$, and the equations can be integrated with high numerical accuracy.

In order to evaluate $\underline{G}^\pi(t)$ it is necessary to evaluate both direct matrix elements (involving the overlap of functions centered about the same proton) and exchange matrix elements (involving the overlap of functions centered about different protons.) The direct matrix elements were evaluated rapidly by using a recurrence relation for the Sturmian functions. The same recurrence relation was used to develop a method for evaluating the exchange matrix elements rapidly. This method has been described in detail in Ref. 3.

The matrix $\underline{N}^\pi(t)$ was inverted by the following iterative procedure, suggested in a somewhat different form to the author by Lipsky²⁰: Dropping the superscript π temporarily let $\underline{X}_n = \underline{X}(t_n)$ denote the exact inverse of $\underline{N}_n \equiv \underline{N}(t_n)$ at time $t = t_n$. Let $\underline{X}_{n, \text{tr}}$ denote a trial estimate of \underline{X}_n . From the identity

$$\underline{X}_n \underline{N}_n \underline{X}_{n, \text{tr}} = \underline{X}_{n, \text{tr}}$$

we have, denoting the identity matrix by \underline{I} and defining $\underline{\Delta}_n \equiv \underline{I} - \underline{N}_n \underline{X}_{n, \text{tr}}$,

$$\begin{aligned} \underline{X}_n &= \underline{X}_{n, \text{tr}} [\underline{N}_n \underline{X}_{n, \text{tr}}]^{-1} \\ &= \underline{X}_{n, \text{tr}} [\underline{I} - \underline{\Delta}_n]^{-1} \\ &= \underline{X}_{n, \text{tr}} \sum_{j=0}^{\infty} (\underline{\Delta}_n)^j. \end{aligned} \quad (\text{A4})$$

If $\underline{X}_{n, \text{tr}}$ is a good approximation to \underline{X}_n the elements of the matrix $\underline{\Delta}_n$ are small and the sum in the last step of Eq. (A4) can be approximated well by the first few terms. In the calculations reported here $\underline{X}_{n, \text{tr}}$ was chosen to be

$$\underline{X}_{n, \text{tr}} = \underline{X}_{n-1} + (t_n - t_{n-1}) \left. \frac{d\underline{X}(t)}{dt} \right|_{t=t_{n-1}}, \quad (\text{A5})$$

where t_{n-1} is the time point previous to t_n . Noting that⁴

$$i \frac{d\underline{N}(t)}{dt} = \underline{M}^\dagger(t) - \underline{M}(t), \quad (\text{A6})$$

the derivative of $\underline{X}(t)$ is given by

$$i \frac{d\underline{X}(t)}{dt} = \underline{G}(t) \underline{X}(t) - [\underline{G}(t) \underline{X}(t)]^\dagger. \quad (\text{A7})$$

The trial estimate was improved by retaining the first three terms in the sum of Eq. (A4). The iteration was begun at a large negative time (see below), where $\underline{X}(t)$ was approximated very accurately by the identity matrix.

The exchange matrix elements were integrated along the projectile path by numerical quadrature, as described in Ref. 3; the integration was begun at $vt = -120$ a.u. The integration of Eqs. (1.8) for $O^\pi(t, -T)$ was performed with a fifth-order Runge-Kutta-type method developed by Lawson, as described by Lapidus and Seinfeld²¹; the integration was begun at $vt = -vT = -60$ a.u. Although Runge-Kutta-type methods are generally thought to be inefficient, it should be noted that Lawson's method has a particularly large region of stability in the complex plane. This means that a large step size can be used to integrate the complex equations for $O^\pi(t, -T)$ without the solution becoming unstable. In contrast, most other methods have a narrow region of stability in the complex plane, and it is often essential to use a small step size when integrating complex equations. For this reason Lawson's method may well be superior to most methods for integrating Eqs. (1.8). The integration was started with a mesh in which t changed by increments of 0.25 a.u. The mesh size was halved whenever the condition

$$\underline{O}^\pi(t, -T)^\dagger \underline{N}^\pi(t) \underline{O}^\pi(t, -T) = \underline{I} \quad (\text{A8})$$

was violated beyond a certain level of tolerance.

The vector $\vec{A}^\pi(T)$ was found from Eq. (1.10). Each element of $\vec{A}^\pi(-T)$ corresponding to exchange

was set equal to zero and each element corresponding to excitation was approximated by the leading term in an asymptotic expansion, with the boundary condition that only the ground state was populated at $t = -\infty$. However, $\vec{A}^r(-T)$ was normalized to unity. The accuracy of the numerical integration was such that $\vec{A}^r(T)^\dagger \vec{A}^r(T)$ deviated from unity by less than 10^{-5} ; in most cases the deviation from unity was substantially less than 10^{-5} .

After $\vec{A}^r(T)$ had been found, $\vec{A}^r(\infty)$ was found by first integrating Eqs. (1.4) for $\vec{A}^r(t)$, starting at $t = T$. The exchange matrix elements appearing

in $\underline{G}^r(t)$ were set equal to zero for $t > T$. The integration was stopped at a certain point $t = T_\infty$, and the difference $\vec{A}^r(\infty) - \vec{A}^r(T_\infty)$ was estimated from the leading term in an asymptotic expansion. A suitable value for T_∞ was found by an extrapolation procedure similar to the one used by Cheshire *et al.*⁶

The computing time required to perform the present 12-state calculations was roughly the same as that required by Cheshire *et al.*⁶ to perform their seven-state calculations, that is, on the average about 20 min for one impact parameter and energy on an IBM 360/65.

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¹See, for example, L. Wilets and S. J. Wallace, *Phys. Rev.* **169**, 84 (1968).

²D. F. Gallaher and L. Wilets, *Phys. Rev.* **169**, 139 (1968).

³R. Shakeshaft, *J. Phys. B* **8**, 1114 (1975).

⁴T. A. Green, *Proc. Phys. Soc. Lond.* **86**, 1017 (1965).

⁵R. Shakeshaft, J. Macek, and E. Gerjuoy, *J. Phys. B* **6**, 794 (1973).

⁶I. M. Cheshire, D. F. Gallaher, and A. J. Taylor, *J. Phys. B* **3**, 813 (1970).

⁷D. G. M. Anderson and M. J. Antal, *J. Phys. B* **8**, 1507 (1975). These authors use a new interpolation scheme which is sufficiently accurate to permit $\underline{G}^r(t)$ to be stored on an unusually sparse mesh.

⁸I. H. Zimmerman, Ph.D. thesis (University of Washington, 1972) (unpublished).

⁹In Ref. 3, and in the paper by R. Shakeshaft and L. Spruch, *Phys. Rev. A* **10**, 92 (1974), it was incorrectly stated that the estimate $P'_{R\alpha, \text{tr}}$ is not variational.

¹⁰J. T. Park, J. E. Aldag, and J. M. George, *Phys. Rev. Lett.* **34**, 1253 (1975).

¹¹H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford U. P., New York, 1952), p. 450.

¹²I. M. Cheshire, *J. Phys. B* **1**, 428 (1968).

¹³G. L. Lockwood and E. Everhardt, *Phys. Rev.* **125**,

567 (1962).

¹⁴J. E. Bayfield, *Phys. Rev.* **185**, 105 (1969).

¹⁵See, e.g., R. M. Drisko, Ph.D. thesis (Carnegie Institute of Technology, 1955) (unpublished); K. Dettmann and G. Leibfried, *Z. Phys.* **218**, 1 (1969); R. Shakeshaft and L. Spruch, *Phys. Rev. A* **8**, 206 (1973).

¹⁶L. H. Thomas, *Proc. R. Soc. A* **114**, 561 (1927); R. Shakeshaft, *J. Phys. B* **7**, 1059 (1974).

¹⁷J. T. Park, J. E. Aldag, J. M. George, J. L. Peacher, and J. H. McGuire (unpublished).

¹⁸D. R. Bates and G. Griffing, *Proc. Phys. Soc. Lond.* **A 66**, 901 (1953).

¹⁹The choice of $f(\vec{R})$ is arbitrary to the extent that it must be real so that $H(t)$ is Hermitian. The arbitrariness arises from the fact that within the impact-parameter approximation the nuclei are assumed to be infinitely massive, so that \vec{R} connects the centers of mass of the colliding systems. Therefore $f(\vec{R})$ is an interaction which depends only on the coordinate connecting the centers of mass of the colliding systems and hence cannot directly induce transitions. Neither can $f(\vec{R})$ influence the probability of a transition through its effect on elastic scattering, since there is assumed to be no elastic scattering. It follows that $f(\vec{R})$ cannot contribute at all to the probability of a transition, and therefore it can be chosen arbitrarily. As is well known, this result can be rigorously demonstrated by absorbing $f(\vec{R})$ into the phase of the trial wave function.

²⁰L. Lipsky (private communication).

²¹L. Lapidus and J. H. Seinfeld, *Numerical Solution of Ordinary Differential Equations* (Academic, New York, 1971).