Excitation and charge transfer to 2s and 2p states in 1—20-keV H^+-H collisions

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Electron excitation and transfer to 2s and 2p states in H^+-H (1s) collisions is studied in the energy range from 1 to 20 keV with the use of a modified two-center atomic-expansion method. It is shown that the inclusion of united-atom orbitals, in addition to the atomic orbitals of the separated atoms, in a two-center expansion allows for the extension of this method to the low-collision-energy regime. The results of our calculations at low energies from 1 to 5 keV agree with experiments and with the recent multistate molecular-orbital calculations by Kimura and Thorson but differ from the molecular-orbital calculations by Crothers and Hughes. At higher energies our results agree qualitatively with experiments and confirm the dip in 2s and 2p excitation cross sections at $E \sim 11$ keV. The impact-parameter dependence of excitation and capture probabilities is also examined to illustrate the evolution of the excitation mechanism from the rotational coupling at lower collision energies to the direct excitation process at higher energies.

I. INTRODUCTION

Excitation and charge-transfer processes in $H^+ + H(1s)$ collisions at intermediate and low energies have been actively studied both experimentally[1–5] and theoretically in the last decade. In the energy region where the projectile velocity is comparable to the electron orbital velocities, expansions of the time-dependent electronic wave function in terms of traveling atomic orbitals have often been used within the framework of the semiclassical impact-parameter close-coupling method. At lower energies, the molecular-state expansion is more appropriate. Both methods have been used extensively in calculating excitation and charge-transfer cross sections in $H^+ + H(1s)$ collisions.

In recent years, careful consideration has been given to including the momentum-transfer effect by electron translation factors (ETF's) in molecular-state calculations. The conventional perturbed-stationary-state (PSS) model neglects these effects and introduces unphysical boundary conditions leading to spurious long-range couplings. Various forms of ETF's have been proposed in recent years by several authors, based either upon intuitive physical considerations[6,7] or upon some variational principles.[8–12] In prototype studies, both Crothers and Hughes[8] and Kimura and Thorson[9] have proposed different forms of variationally determined ETF's and applied these in ten-state molecular-orbital expansions to calculate excitation and charge transfer to 2s and 2p states from 1 to 7 keV in $H^+ + H(1s)$ collisions. Not surprisingly, their results are rather different from those of earlier PSS calculations[13] where ETF's were not included. Unfortunately, however, these two sophisticated calculations lead to conflicting results in the 2s excitation and charge-transfer cross sections, although the 2p excitation and charge-transfer cross sections are essentially identical. Comparison with experiments does not provide any clear-cut guidance either. There are few experimental data for 2s excitation cross sections in the 1 to 5 keV region. For 2s capture, the results of Crothers and Hughes appear to be in agreement with the early data of Bayfield.[4] On the other hand, the results of Kimura and Thorson agree better with the measurements of Hill *et al.*[3] and of Morgan *et al.*[1,2]

Extension of the molecular calculations to higher energies meets conceptual as well as practical problems. The atomic-orbital (AO) expansion model[14] which has been widely used in the intermediate- and high-energy regions might be considered to provide for a better method of studying excitation and charge transfer to 2s and 2p states around 25 keV. But results from earlier multistate two-center atomic-expansion calculations[14] do not show good agreement with experiments around and below 25

keV. In the energy range from about 5 to 25 keV, the $H^+ + H$ collision seems to be too fast to follow a predominantly quasimolecular development of the system, but too slow for being approximated in terms of a few undistorted atomic orbitals.

In a recent article[15] we developed a modified two-center atomic-orbital expansion model (denoted as AO + model) for studying inelastic collisions in the intermediate- and low-velocity regions. Recognizing that the failure of the conventional two-center AO expansion is due to the poor representation of united-atom (UA) orbitals by the bound spectrum of the separated atoms (SA), in the AO + model we *explicitly* incorporate relevant UA orbitals into the two-center AO expansion. As the choice of UA orbitals is guided by the molecular correlation diagram, the system is allowed to develop like a quasimolecular system in close collisions at low velocities. In fact, it will be shown below that the static molecular correlation diagram is well reproduced when diagonalizing the two-center Hamiltonian in an appropriate AO + expansion but not in an expansion in terms of bound SA orbitals (LCAO method). By applying the AO + model in dynamic calculations over a broad velocity range we have demonstrated in Ref. 15 that this model is well applicable to collisions at intermediate as well as at low velocities. In Ref. 15 we have compared the results of AO + calculations for the total electron transfer cross sections in $H^+ + He^+$ collisions with those from coupled multistate molecular calculations. At small collision velocities the AO + results were shown to be in good agreement with the molecular-orbital (MO) calculations of Winter and Hatton.[16] At higher energies the AO + results were found to differ from the MO results but the discrepancy has been attributed[15,17] to the lack of convergence in the MO expansion.

In this article, we apply the AO + model to study charge transfer and excitation to $2s$ and $2p$ states in $H^+ + H$ collisions from 1 to 20 keV. We show that our results are in good agreement with the molecular calculations of Kimura and Thorson[9] but differ from the similar molecular calculations of Crothers and Hughes[8] from 1 to 5 keV. At 7 keV, the highest energy where molecular calculations have been performed, there appears to be a lack of convergence in the ten-state MO expansion. We will also show that our AO + calculations confirm convincingly the existence of a dip structure in the $2s$ and $2p$ excitation cross sections around 11 keV. These structures have been observed in experiment[1] but have not been confirmed unequivocally in theoretical calculations previously.

II. AO + MODEL AND H_2^+ CORRELATION DIAGRAM

In the present work we adopt the semiclassical impact-parameter formulation of the close-coupling method, assuming straight-line trajectories for the heavy particles. The time-dependent electronic wave function is expanded as

$$\psi(\vec{r},t)=\sum_j a_j^A(t)\phi_j^A(\vec{r}_A)\exp[-i(-\tfrac{1}{2}\vec{v}\cdot\vec{r}+\tfrac{1}{8}v^2t+\epsilon_j^A t)]+\sum_k a_k^B(t)\phi_k^B(\vec{r}_B)\exp[-i(\tfrac{1}{2}\vec{v}\cdot\vec{r}+\tfrac{1}{8}v^2t+\epsilon_k^B t)]\ . \tag{1}$$

In Eq. (1) $\vec{r}$, $\vec{r}_A$, $\vec{r}_B$ denote the electronic coordinate referred to, respectively, the midpoint of the internuclear axis and the atomic centers, A, B; $\vec{v}$ is the constant collision velocity on a classical straight-line trajectory, $\phi_n^c(\vec{r}_c)$; $c=A,B$ are some atomic basis states; the energies ϵ_n^c are the expectation values of the atomic Hamiltonians H_c between the basis states; and $a_n^c(t)$ denote the time-dependent occupation amplitudes of traveling states n, to be determined by solving the standard coupled-state equations. The velocity-dependent phase factors are the familiar plane-wave electron translation factors in the two-center AO expansion where the origin of the collision system has been chosen to be at the midpoint of the internuclear axis.

In the present AO + calculations, 22 atomic states were included, consisting of $1s$, $2s$, $2p_0$, and $2p_{\pm1}$ orbitals[18] of the separated atom and of the united atom in the two centers (16 altogether), plus $3d_0$, $3d_{\pm1}$, and $3d_{\pm2}$ orbitals of the united atom, also around the two centers. The $3d$ orbitals of the united atom are included since the $3d\sigma$ molecular orbital correlates to the $2p_0$ orbital in the separated-atom limit. In Fig. 1 we show the important adiabatic molecular potential curves relevant to the present collision study and the comparison with potentials calculated in the AO + model (shown as crosses). Except for the small deviations for the $3d\sigma$ curve at small R, we notice that all these molecular potential curves are well reproduced by

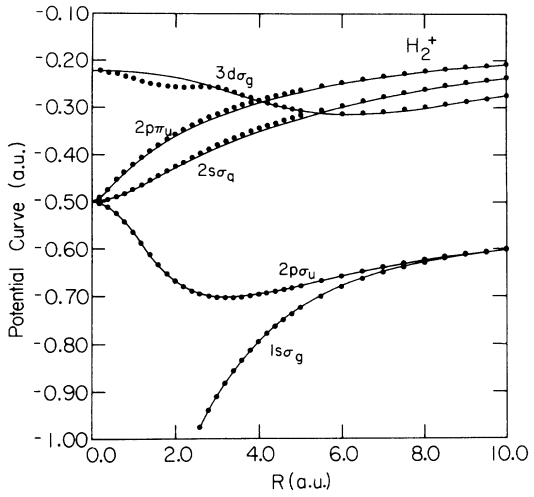

FIG. 1. Lowest five molecular potential curves of H_2^+. The solid lines are exact results and the solid circles are the results from diagonalizing the electronic Hamiltonian in the 22 AO + basis set.

the present AO + model throughout the whole range of internuclear separations shown. Such close agreement is important if the AO + model is to be applicable to slow collisions.

Having defined the basis set, the solution of the coupled differential equation is straightforward. We only note that the UA orbitals are orthogonalized to the bound SA orbitals at the respective collision centers to facilitate the formulation of boundary conditions. Incidentally, this procedure results in SA energy expectation values in the continuum, implying that some continuum contributions have been included in the AO + expansion. In this respect the AO + model is similar to the pseudostate expansion of Cheshire *et al.*,[19] and to the Sturmian basis expansions.[20] However, it is emphasized that the pseudostates used in the AO + model are to allow the system to relax towards the UA limit in close collisions at low velocities. When such binding effects are not important, such as in collisions at large impact parameters or collisions at higher velocities, the pseudostates (the UA orbitals) included in the AO + model are not relevant, i.e., the amplitudes $a(t)$ for these states remain small throughout the collision. At intermediate energies, SA orbitals are important in describing distant collisions but UA orbitals are needed for describing the relaxation of the system at close collisions. Without these UA orbitals or orbitals of similar characters, the two-center atomic-expansion method will not be useful for close collisions at intermediate- and lower-collision velocities. Although the UA orbitals contain some higher SA orbitals to a certain degree, the present AO + model is not expected to be useful at high energies when excitation to higher states ($n > 3$) and ionization become important.

III. RESULTS AND DISCUSSION

A. Total cross sections

Cross sections for excitation and charge transfer to $2s$ and $2p$ states for $H^+ + H$ are shown in Figs. 2(a)–2(d) over the energy range from 1 to 25 keV.[21] In Fig. 2(a), excitation cross sections to the $2s$ state measured by Morgan *et al.*[1] are shown together with the results of several theoretical calculations. The AO + model gives results in reasonably good agreement with the data of Morgan *et al.*[1] over the whole energy range displayed except for $E > 15$ keV. It predicts a small dip for $E \sim 11$ keV. This dip appears to be consistent with experimental data. The AO + results are in harmony with the ten-state MO calculations of Kimura and Thorson[9] for $E = 1-5$ keV but differ substantially from a ten-state molecular calculation by Crothers and Hughes.[8] These two groups employed the same set of MO states but different forms of electron translation factors in their calculations. It has been stated by Kimura and Thorson that the discrepancy between the two MO calculations cannot be proved to be due to the difference in the ETF's.[22] Also shown for $E > 15$ keV are the experimental data of Park *et al.*[5] which are essentially in agreement with the results of Morgan *et al.* The open circles are from the pseudostate calculations of Cheshire *et al.*[19] Their pseudostates are not chosen to represent the UA limit sufficiently well, and their results, therefore, scatter somewhat around MO or AO + results.

Capture cross sections to the $2s$ state are shown in Fig. 2(b). Except for the lower energies the data of Morgan *et al.*[1,2] are essentially in agreement with the data of Hill *et al.*[3] These data are well reproduced by the AO + calculations in the whole energy range displayed and by the MO calculations of Kimura and Thorson[9] from 1 to 7 keV. The experimental data of Bayfield[4] appear to be too low and the calculation of Crothers and Hughes[8] shows a minimum at $E \sim 4$ keV not present in the other two experiments nor in the other calculations shown.

In Fig. 2(c), cross sections for excitation to the $2p$ state are shown. The trend of the experimental data of Morgan *et al.*,[1] including the dip around 11 keV,

are well confirmed by the AO + calculation. At lower energies, the two MO calculations and the AO + results are all in harmony for $E=1-5$ keV. However, the agreement between the results of Crothers and Hughes with AO + and with Kimura and Thorson might be misleading. From the polarization fraction of the 2p deexcitation reported in Ref. 8, excitation cross sections to $2p_0$ and $2p_{\pm 1}$ calculated by Crothers and Hughes are different from the results of AO + and of Kimura and Thorson (see the second paragraph below). At $E=7$ keV, the MO results appear to be too high. The MO cross sections do not appear to decrease with increasing energies, in contradiction with experimental data and with the AO + results. It seems that the MO calculation at 7 keV is not fully converged.

The 2p capture cross sections are displayed in Fig. 2(d). The experimental data of Morgan *et al.*[1] constitute the only known measurement. For small collision energies, the results from the two MO calculations and from the AO + calculations are in

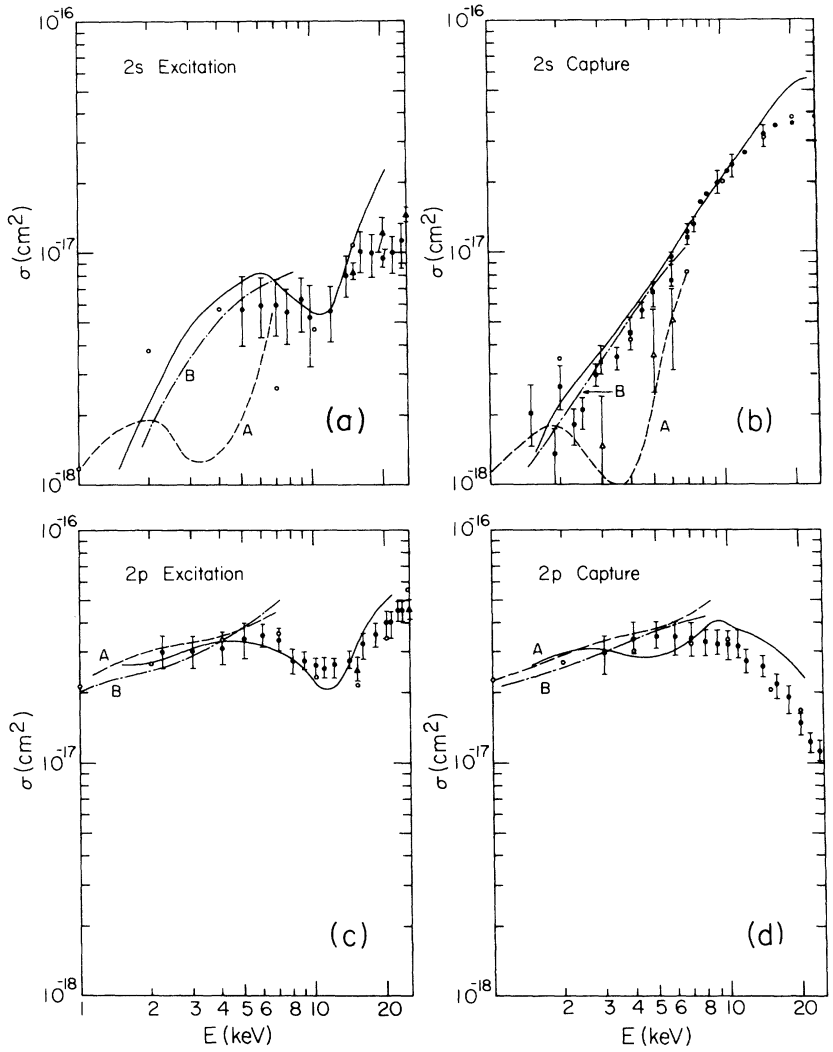

FIG. 2. Total cross sections for direct and charge transfer to 2s and 2p states in H^+-H (1s) collisions from 1 to 25 keV. Theoretical calculations: solid lines, present AO + results; curve A (dashed lines), MO results of Crothers and Hughes; curve B (dash-dot lines), MO results of Kimura and Thorson. Experimental data: ♦, Morgan *et al.* (Ref. 1). In (a) and (c), the ▲ results are from Park *et al.* (Ref. 5), renormalized according to Shakeshaft (Ref. 26) and using the 2s/2p ratio calculated by Shakeshaft. In (b), ♦ from Hill *et al.* (Ref. 3); △ from Bayfield (Ref. 4). The open circles are from the pseudostate calculations of Cheshire *et al.* (Ref. 18).

good agreement except that the AO+ model predicts a small drop (about 10%) for $E \sim 5$ keV. At higher energies, the AO+ model predicts higher cross sections than experimental results (about 50% at 20 keV).

In Table I the calculated total cross sections to each atomic $2s$, $2p_0$, and $2p_{\pm 1}$ states are tabulated. The polarization fraction P, defined as[23]

$$P=\frac{\sigma(2p_0)-\sigma(2p_{\pm 1})}{2.375\sigma(2p_0)+3.749\sigma(2p_{\pm 1})}, \quad (2)$$

for excitation to $2p$ are also shown. Our calculated polarization fractions differ from the experimental results of Kauppila *et al.*[24] They are also in disagreement with the calculations of Crothers and Hughes reported in Ref. 8(c) in the 3–7-keV region. While our results in the 1–5-keV region show that P is almost constant, in agreement with the results of Kimura and Thorson, the results of Ref. 8(c) show a rapid variation with energy in the 3–7-keV region. The experiment reported a near-zero value for P in the 1–5-keV region. This is at variance with the molecular model which predicts a value of -0.267 in the low-energy limit.

B. Impact-parameter dependence

The collision dynamics vary tremendously over the energy region considered in this article. For energies below 5 keV, the collision velocity is relatively slow such that an expansion in a molecular basis is appropriate. If a quasimolecular complex is indeed transiently formed in slow collisions such that the initial linear momentum carried into the collision by the electron is not crucial, then excitation and charge-transfer cross sections to the same state (e.g., $2s$ or $2p$) are expected to be about the same for symmetric collisions. (The linear momenta as represented by the ETF's are *always* needed in specifying correct asymptotic boundary conditions independent of collision velocities.) At such low energies, transitions from $1s\sigma_g$ MO to higher MO's are small. Instead, transitions through the highly promoted $2p\sigma_u$ MO at small internuclear separations are more effective. Referring to Fig. 1, the $2p\sigma_u - 2p\pi_u$ rotational coupling near the united-atom limit constitutes the major excitation mechanism at small collision energies, while the $1s\sigma_g - 2s\sigma_g$ radial coupling is much weaker (to a certain extent, the higher MO's also participate). From the nature of the excitation mechanism it is thus expected that all nonresonant inelastic processes at small collision velocities occur at small impact parameters and that the breakup into excitation and charge-transfer channels of the same atomic states is nearly identical. These features are certainly exhibited in the total cross sections in the MO calculations of Kimura and Thorson as well as in the AO+ model (see Table I).

To show the comparison in more detail, we illus-

TABLE I. Direct- and charge-transfer cross sections to $2s$, $2p_0$, and $2p_{\pm 1}$ states in $H^+ + H(1s)$ collisions calculated in the AO+ model. The cross sections are given in units of 10^{-18} cm^2. Also shown are the polarization fractions [defined as in Eq. (2)] for $2p$ excitations.

	Excitations				Capture		
E (keV)	$2s$	$2p_0$	$2p_{\pm 1}$[a]	P	$2s$	$2p_0$	$2p_{\pm 1}$[a]
1.56	1.25	0.74	25.8	−0.243	1.19	0.77	25.7
2.00	2.24	0.82	26.4	−0.241	2.13	0.87	27.8
3.00	4.72	1.22	29.3	−0.232	3.68	1.22	27.8
4.00	6.38	1.97	31.4	−0.216	5.32	1.31	25.8
5.16	7.66	2.00	29.4	−0.212	7.48	1.32	25.8
6.00	7.92	2.35	26.9	−0.198	9.58	2.42	27.7
7.00	7.72	3.56	23.4	−0.156	12.6	3.80	30.4
7.71	6.76	5.33	22.0	−0.105	13.7	4.56	31.6
8.65	5.82	6.79	19.5	−0.056	15.1	7.01	33.0
11.11	5.24	8.77	9.89	0.097	21.6	14.0	30.6
15.0	11.4	14.5	19.3	0.069	35.6	12.6	19.0
20.0	22.1	28.2	22.2	0.158	52.5	11.8	11.7

[a]Sum of $2P_{+1}$ and $2P_{-1}$ cross sections.

trate in Fig. 3 the impact-parameter-weighted excitation (solid lines) and charge-transfer (in dashed lines) probabilities $bP(b)$ versus impact parameters b. For $E=1.563$ keV [Fig. 3(a)] the excitation and charge-transfer probabilities to the same state are essentially identical and cannot be distinguished in the graph. Since the $2p\sigma_u-2p\pi_u$ rotational coupling is much more important than radial couplings at this energy, excitation and charge transfer to $2p$ (mostly due to $2p_{\pm1}$) are much stronger than to $2s$. As the collision energies increase, the probabilities tend to peak and shift to larger impact parameters. For energies between 3 and 7 keV, the degree of agreement between excitation and transfer probabilities decreases as the linear momentum carried by the electron into the collision is "remembered," particularly for collisions occurring at larger impact parameters. In Figs. 3(b) and 3(c), $bP(b)$ vs b are shown for $E=4$ and 6 keV, respectively. At these energies excitation and charge transfer begin to deviate from each other. The effects are first felt by the small $2s$ channels.

For E greater than 7 keV, the collision is too fast for the electron to experience a significant number of oscillations between the two centers. The description of collision dynamics in terms of the promotion of molecular orbitals becomes less important. In Figs. 4(a)–4(e) we show the $bP(b)$ vs b at five higher energies. We notice that the deviation of charge-transfer probabilities from capture probabilities are large and that the contribution of probabilities to the total excitation cross sections from large impact parameters is significant. Notice the increase of the range of important impact parameters in Fig. 4 with increasing energies. Not only that capture and excitation probabilities are not similar, but the dependence on b for each channel varies rapidly within a short range of energies. For example, $2p$ excitation probabilities drop rapidly in the 7–11-keV range. The shape of $P(b)$ changes from that characteristic of $2p\sigma_u-2p\pi_u$ rotational coupling at 7 keV (and lower) to the more irregular one at 11 keV. For $E\geq15$ keV, contributions from large impact parameters (through direct excitation) become dominant. Thus energies around $E=11$ keV appear to form a dividing line for the two mechanisms. The dip in $2p$ excitation cross sections at $E=11$ keV may thus be interpreted as the result of a drop of the rotational coupling mechanism before the direct excitation mechanism picks up. The variation of $2p$ capture is less dramatic. Its $P(b)$ always remain relatively small at large impact parameters, even at higher velocities.[25] This is characteristic of capture probabilities which shift to small

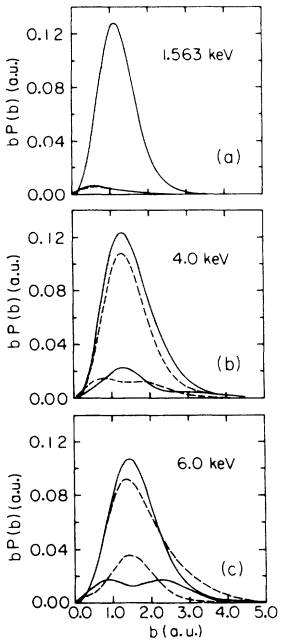

FIG. 3. Impact-parameter-weighted probabilities $bP(b)$ for $2s$ and $2p$ excitation and charge transfer vs impact parameters b for H^+-H $(1s)$ collisions at $E=1.561$, 4, and 6 keV. $2p$ excitations, upper solid lines; $2s$ excitations, lower solid lines; $2p$ capture, upper dashed lines; $2s$ capture, lower dashed lines.

impact parameters as energies increase. The $P(b)$ for $2s$ excitation also shows changes at $E\sim11$ keV similar to that for $2p$ excitation. For $E<11$ keV, contributions to the total cross sections come mostly from small b. For $E>11$ keV, contributions from large b become important, signifying the dominant direct-excitation mechanism.

IV. SUMMARY

In this article we illustrate the application of the AO+ model in the calculation of excitation and charge transfer to $2s$ and $2p$ states in the energy range from 1 to 20 keV in $H^+ + H$ collisions. It is shown that existing experimental data are in reasonably good agreement with the present calculations, although several features predicted by the AO+ model are only qualitatively confirmed by experiments. We have also shown that our results at small collision energies $E\leq5$ keV are in good agreement with the recent multistate molecular calculations of Kimura and Thorson but differ from similar molecular calculations of Crothers and Hughes.

We emphasize the importance of united-atom or-

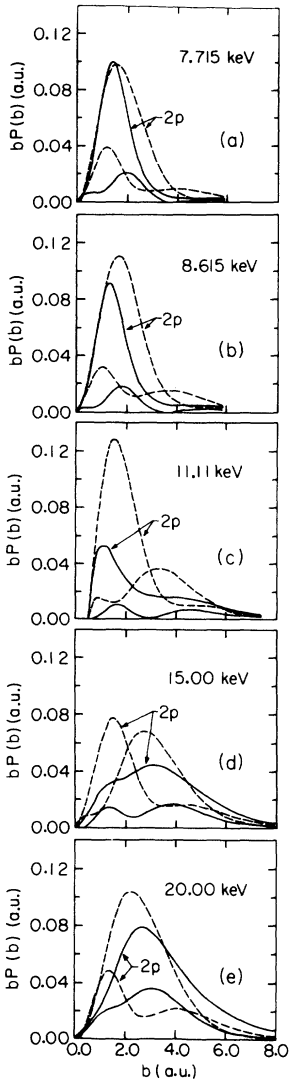

FIG. 4. Same as in Fig. 3 except at $E=7.715$, 8.65, 11.1, 15, and 20 keV. Solid lines are for excitations and dashed lines are for capture, with $2s$ or $2p$ as labeled.

bitals in the AO+ model for reproducing the "molecular features" in applying a two-center AO expansion to collisions at lower energies. Even in the intermediate energy region, these UA orbitals are important for collisions at small impact parameters. For the system studied in this article, the present investigation provides the first reliable calculations for $2s$ and $2p$ excitation and charge transfer from 7 to 20 keV. At lower energies, the present investigation offers a unique independent alternative to the molecular coupled-state calculations. It might, therefore, as in the present case, contribute to the understanding of conflicting results from large-scale MO studies without actually launching another conflict of similar type. Although about twice as many states are needed in the present AO+ expansion than in the MO expansion to account for the same number of molecular channels, calculations in the AO+ model are actually very efficient since all the matrix elements are smooth functions in contrast to the coupling matrix elements in the molecular expansions, thus making the AO+ model a viable approach to ion-atom collisions at lower energies.

Because of the nature of the UA orbitals used in the present AO+ model, this model gradually becomes not suitable for collisions at $E \geq 20$ keV. At higher collision energies, excitation to higher states and ionization are not negligible, but these channels are not represented in the present AO+ model. To calculate excitation and charge transfer to $2s$ and $2p$ states accurately in the higher-energy region within the close-coupling method, these high-lying states have to be included explicitly. Although the orthogonalized UA orbitals in the present AO+ model have energy expectation values in the continuum, these states lie too far away from the ionization threshold. To represent the most important low-lying continuum states in the ionization channel, other pseudostates with energy expectation values near the ionization threshold have to be used. The AO+ model definitely allows for this possibility, but this is a subject for future study.

Note added in proof. After this paper had been accepted, the authors received a preprint by H. J. Lüdde and R. M. Dreizler (unpublished) where excitation and charge transfer to $2s$ and $2p$ states were studied in the 1–50-keV region. These authors solved the time-dependent Schrödinger equation by expansion in a pseudobasis set of the Hylleraas-type. For the excitation cross sections to $2s$ and $2p$ states, they also predicted a dip at $E \sim 11$ keV. Our results for excitation to $2p$ are in good agreement with their results, but deviations exist for the excitation to $2s$ where our results agree better with experiments.

ACKNOWLEDGMENTS

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