Atomic-orbital-expansion studies of electron transfer in bare-nucleus Z ($Z=2,4-8$) –hydrogen-atom collisions

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The atomic-orbital-expansion description has been employed in calculations of electron transfer in ${}_zX^{Z+}+H$ collisions ($Z=2,4-8$) in the energy range 0.1–30 keV/amu. Total transfer cross sections have been determined as well as partial cross sections for transfer into individual n,l subshells of the projectile. Results are compared to those derived with other methods and to available experimental data. Generally, qualitative agreement is found between results of the present study and those calculated with other close-coupling schemes. Quantitatively good agreement is found in cases where other studies based on large-scale computations are available, i.e., for $C^{6+}+H$ and $O^{8+}+H$ collisions. But even in these cases, the results from the most involved calculations appear to have converged towards each other for the dominant partial cross sections only.

I. INTRODUCTION

In studies of electron transfer in ion-atom collisions, systems with highly charged projectiles have attracted increasing attention[1] within the recent past. Newly developed ion sources have produced bare projectile nuclei with charge numbers Z ranging up to 10 at keV or even eV energies. Improved detection techniques aim at the determination of partial cross sections for transfer into individual n,l subshells of the projectile. On the theoretical side, model descriptions and calculational methods have been improved. Moreover, much progress has come with the availability of fast computers which are capable of handling the large number of mutually interdependent channels involved in slowly colliding, highly charged systems. The developments in both experiment and theory have been furthered by the practical interest taken in such collision systems by the plasma and the laser physics community.

In this paper we present and discuss calculated cross sections for electron transfer into individual n,l and into all shells of the projectile, in collisions between bare projectiles and hydrogen atoms in the energy range of 0.1–30 keV/amu, with $Z=2$ and 4–8. (The $Li^{3+}+H$ system, $Z=3$, is not included since it has been covered extensively in the literature, see references in Salin's work.[2]) In theoretical studies, such one-electron systems are particularly attractive since their respective Hamiltonians as well as their initial and final electronic orbitals are known exactly. From a numerical viewpoint, however, they constitute an intricate problem since low-energy capture leads to selective population of high-n orbitals. In the cases considered here where transition probabilities are large and perturbation methods fail, therefore, one is faced with the problem of many closely coupling channels. The convergence of calculations which necessarily involve large-scale computations often cannot be tested by further enlargement of the number of channels included. Rather, the accuracy of results may be assessed by comparison between predictions of various model descriptions and experimental data.

A considerable number of theoretical studies in the field under investigation has been published recently. At present, the most complex investigations are those by Green *et al.*[3] for $C^{6+}+H$ and by Shipsey *et al.*[4] for $O^{8+}+H$ collisions, both based on expansions of the time-dependent electronic wave function into a large set of traveling molecular orbitals (MO) and the solution of the semiclassical coupled equations. These investigations show that earlier few-state MO studies by Harel and Salin[5] and by Vaaben and Briggs[6] had correctly identified the main transfer mechanisms but had failed to lead to satisfactory quantitative results. In other investigations[7,8] of $C^{6+}+H$ and $O^{8+}+H$ collisions using MO expansions of more limited size, Salop and Olson have presented total transfer cross sections which are close to the results of the involved studies.[3,4] Due to the lack of translational factors in these investigations,[7,8] however, detailed information like partial cross sections could not be extracted. Of the less asymmetric systems, $Li^{3+}+H$, $Be^{4+}+H$, and $B^{5+}+H$ have been studied[9] very recently with a set of traveling MO by Kimura and Thorson. These systems as well as the $He^{2+}+H$ system have been studied by Lüdde and Dreizler[10] above 4 keV/amu with an expansion into a large set of Hylleraas basis functions. Systems with $Z\geq 5$ have been investigated by Janev *et al.*[11] below 3 keV/amu on the basis of the multichannel Landau-Zener theory. All of these systems have been studied within the unitarized distorted-wave approximation[12] (UDWA) over a broad range of energies.

Generally, total transfer cross sections from these methods agree only within roughly a factor of 2 while information on partial transfer cross sections is scarce. Clear-cut experimental evidence in favor of one or another

of the calculated results is still missing. Measured partial transfer cross sections are not yet available but are likely to emerge in the near future. Therefore, while calculated total transfer cross sections clearly need confirmation by applying alternative methods, there is need for a theoretical determination of partial transfer cross sections. Even in the large-scale MO studies there is some uncertainty[3,4] as to the accuracy of the reported results at the high-energy end where MO expansions are less appropriate.

The calculations reported here are based on a two-center expansion of the time-dependent electronic wave function in atomic orbitals (AO). Such expansions have been known[13] for a long time to provide for an adequate description of collision processes at intermediate velocities v, $v/v_e \simeq 1$ (v_e is electronic orbital velocity), or, rather,[14] of distant collisions which take place at those velocities. Recently it has been realized[15] that modified AO expansions (AO + expansions) can be also applied to low-energy collisions, when molecular binding effects in close collisions are taken into account by including *united-atom* (UA) orbitals at the two collision centers. In investigations[15,16] of the highly model-sensitive partial cross sections for population of $2s$ and $2p$ H orbitals through excitation and transfer in $H^+ + H$ collisions, results from MO studies at low energies have been closely reproduced. Very recently, the impact-parameter-b—dependent transfer probabilities $P_m(b)$ into states with fixed magnetic quantum number m have been calculated[17] by direct numerical integration of the Schrödinger equation, and have been found to closely agree with results of AO+calculations.[18] It has been argued,[15,19] therefore, that such modified AO expansion schemes offer a convenient independent alternative to MO expansions at low energies and allow for the ready continuation of calculations to higher energies beyond the commonly accepted region of validity of MO expansions.

In the AO+ expansion description, the representation of unrelaxed atomic orbitals of the separated atoms (SA) as well as relaxed molecular orbitals (through UA orbitals) is achieved with basis sets which are larger than corresponding MO or conventional AO basis sets. For simple collision systems, the enlarged AO+ basis set is still a very efficient tool in dynamical calculations, particularly due to the smooth structure of the coupling matrix elements between atomic functions. For very asymmetric systems involving many channels, however, the very number of SA and UA orbitals of the AO+ expansion becomes prohibitively large. In the present investigation, therefore, it has not been attempted to employ full AO+ sets in the form described earlier,[15,16] where *all* UA orbitals have been included to which the relevant MO correlate in the limit of vanishing internuclear separations. Rather, conventional AO basis sets are being used here which are complemented by merely a few UA orbitals whenever this seemed necessary and possible. Actually, for systems with increasing projectile charge, the inclusion of UA orbitals may become increasingly redundant, at least if included at the projectile center, since their respective overlaps with the corresponding projectile orbitals become large. Already in $Li^{3+} + H$ collisions, total capture cross sections have been demonstrated[18] to be virtually insensitive to the presence of such UA orbitals in AO+ calculations at energies above 0.2 keV/amu. The same holds true for partial transfer cross sections into those orbitals which are populated in distant collisions, i.e., for the dominant partial cross sections. For example, in low-energy $Li^{3+} + H$ collisions, $n=2$ partial cross sections from the AO+ calculations agree well with those from a conventional AO expansion[20] but $n=3$ partial cross sections do not, as the result of different transfer mechanisms.[19]

The main features of the model description as used in the present investigation and the calculational procedures are summarized in Sec. II. Results of the calculations are presented and discussed in Sec. III. Finally, Sec. IV contains some concluding remarks.

II. THE MODEL

The semiclassical two-center close-coupling method with atomic basis sets (including pseudostates) has been frequently described in the literature, and details of this method need not be repeated here. In this section, we only summarize the main features of the model description and of the calculational procedures as they have been used in the present investigation. For further details, the reader is referred to Refs. 15 and 21, and to references therein.

We start from a two-center expansion of the time-dependent electronic wave function in a set of traveling atomic orbitals. The basis set is taken to consist of orbitals of colliding "separated atoms" (ions) H and ${}_Z X^{(Z-1)+}$, as it is commonly done in conventional AO expansion studies,[1,3] as well as those of the "united atom" (ion) ${}_{(Z+1)}X^{Z+}$, positioned at the traveling collision centers. The latter, tighter bound orbitals are needed in a representation of static molecular orbitals in terms of atomic orbitals (LCAO method) at small internuclear separations.[15,19] In dynamical studies within the AO expansion method, they are used for explicitly representing the molecular binding effect in slow or close collisions. All orbitals are assigned either plane-wave translational factors $\exp(i\vec{v}_c \cdot \vec{r})$ in calculations with straight-line trajectories ($\vec{v}_c$ is the velocity of collision center c, $\vec{r}$ the electronic coordinate, atomic units are used throughout this paper if not stated otherwise), or, in studies with curved-line trajectories, modified[21] translational factors $\exp[i\vec{v}_c(t)\cdot\vec{r}]$ which still are of plane-wave form at each instant, but explicitly time dependent due to the time variation of the vector velocity $\vec{v}_c(t)$. For each collision system, the set of basis orbitals has been chosen in an effort to compromise between the requirements of computational economy and of accuracy of results, as will be illustrated below. After separately orthogonalizing the basis sets at each collision center, one arrives at the standard form[13] of coupled differential equations which, however, in the curved-line case, contain an accelerator-dipole term.[21] This latter term, as well as the other coupling terms, has been evaluated with the methods given by McCarroll.[13] Care has been taken to start and to finish the numerical integration of the coupled equations at internuclear separations large enough such that any remaining couplings there are very small. Since, in the AO expansion model, couplings occur between orbitals in a *space-fixed*

coordinate system, the coupled equations need be integrated only in a much smaller range z_0 of the variable $z = vt \leq z_0$ (typically $z_0 \leq 50$ a.u.) than is the case in customary MO studies where long-range rotational couplings of purely geometric origin are usually taken into account by extending the integration to much larger values of z_0. The initial condition can be easily formulated in terms of a single amplitude (that of the H $1s$ orbital). The final occupation amplitudes of basis states are directly the amplitudes for transfer into individual n,l,m basis orbitals of the receding hydrogenlike projectile ion ${}_ZX^{(Z-1)+}$.

III. RESULTS AND DISCUSSION

The problems encountered in theoretical studies of capture in highly-charged-ion—atom collisions are most easily demonstrated for the example of $C^{6+}+H$ collisions. For this collision system, a number of calculations have appeared in the literature, notably, the recent large-scale MO study by Green *et al.*,[3] and low-energy experimental data are available. For this reason, in the following the $C^{6+}+H$ system is discussed in some detail, and it is described how the present model, cf. Sec. II, is applied to this system. The subsequent presentation for the other collision systems is then kept rather short.

A. $C^{6+}+H$

Figure 1 displays part of the molecular correlation diagram for the $C^{6+}+H$ system. Only σ orbitals are shown. In slow collisions, the electron, initially in the atomic $1s$ H state, moves,[3,7] into the interaction zone on the $5g\sigma$ orbital and couples most strongly radially with the $4f\sigma$ orbital near $R=8$ a.u. Once in the $4f\sigma$ orbital, the electron

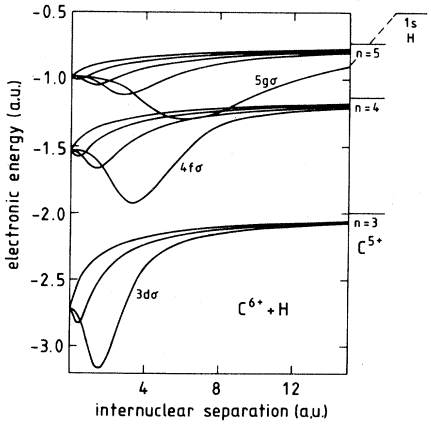

FIG. 1. Molecular energy diagram of σ states in the $C^{6+}+H$ system. States corresponding to the energy curves labeled $4f\sigma$ and $5g\sigma$ are most important for an understanding of low-energy electron transfer within a radial-coupling description.

may be shared with other orbitals correlating to the $n=4$ C^{5+} shell by a multitude of radial and rotational couplings[3,7] or may be further transferred to the $n=3$ C^{5+} shell, particularly by the $4f\sigma$-$3d\sigma$ radial coupling. Population of the $n=5$ C^{5+} is also possible by couplings of the $5g\sigma$ orbital to those orbitals which correlate to the $n=5$ shell, or by couplings of the latter to the adjacent orbitals correlating to the $n=4$ C^{5+} shell. Inclusion of all these 32 molecular orbitals in a coupled-state calculation (with some couplings omitted) has been achieved recently.[3]

In the present investigation which is relevant in the low-to-intermediate energy region, molecular orbitals are represented within the AO+ model, i.e., by atomic orbitals of the separated atoms and the united atom. If, in a full AO+ expansion calculation, MO are to be represented to a high degree of accuracy, particularly, if united-atom orbitals are to be placed at both collision centers as has been done previously,[15,16,18] the number of atomic basis orbitals largely exceeds the corresponding number of molecular orbitals (32 MO for $C^{6+}+H$). Such a procedure seemed to be excessively expensive (although still feasible with present-day facilities) and, moreover, not needed for very asymmetric collision systems for the following reasons.

(i) Low-energy transfer in the currently studied asymmetric collisions occurs, in a first step, mainly through localized couplings between two σ states. For the calculation of *total* transfer, therefore, the corresponding σ states need careful representation only in an outer range of internuclear separations ($R \geq R_0$). If R_0 is sufficiently large, as is the case for the $C^{6+}+H$ system as well as for the other systems under investigation, a purely atomic-orbital expansion (with AO of the separated atoms) offers good representation of those molecular orbitals, in the spirit of the customary LCAO procedure. For this reason, e.g., an AO expansion calculation[21] involving a set of 10 AO ($1s$ H and the $n=4$ C^{5+} orbitals) gives already total transfer cross sections in excellent agreement with the results of the MO calculation.[3]

(ii) For a reliable determination of low-energy *partial* cross sections, the relevant molecular orbitals must be represented to a higher degree of accuracy, and probably at smaller internuclear separations. In asymmetric collision systems, these MO are still given, to a good approximation, by the LCAO method with AO of the separated atoms since even united-atom orbitals (i.e., MO at $R=0$) have large overlaps with the corresponding separated-atom orbitals of the heavier partner.

(iii) A costly better representation of MO at smaller internuclear separations may not be appropriate since, in slow collisions where such modifications may manifest themselves in altered partial cross sections, some ambiguity exists as to how to choose the internuclear trajectory. As has been reported already earlier,[21] total transfer cross sections are found to depend on the internuclear trajectory below 1 keV/amu, with an unscreened internuclear Coulomb potential resulting in cross sections below those from a calculation with straight-line trajectories. This feature of the calculations has been observed for all of the highly asymmetric systems under investigation, the cross sections from the straight-line calculation being up to

double those from the curved-line calculation at 0.1 keV/amu in some cases. These features are qualitatively understood by noting that collisions on curved trajectories lead to more distant collisions which, moreover, occur with diminished velocities. It is, however, hard to give *a priori* reasons for the unique choice of the trajectory in a given low-velocity collision situation. Apparently, a straight-line trajectory can safely be assumed on the incoming path up to the point where transfer sets in. From there on, if the final amplitudes depend on the further course of the trajectory, a self-consistent determination of trajectory and amplitudes would be needed for arriving at accurate results, or even abandonment of the semiclassical picture altogether. In this paper, we restrict ourselves to deriving results in separate calculations for straight-line and for (unscreened) Coulomb trajectories, respectively. The discussion of trajectory effects in connection with results of other investigations is resumed in Sec. IV.

For all these reasons, most calculations for the heavier collision systems ($Z \geq 6$) have been performed with atomic orbitals of the separated atoms only, for the $C^{6+}+H$ system with an AO basis set restricted to 35 AO, the 26 $n=4,5$, C^{5+} orbitals and the $1s$ H orbital, as well as $n=2,3$ H orbitals, the latter originally included in order to study H excitation in those collisions as well. The $n=3$ C^{5+} orbitals have not been included in the basis because transitions into these states are known[3] to be small. With this expansion, the $4f\sigma$ and $5g\sigma$ MO are represented to better than 90% over the whole range of internuclear separations R, and to better than 99% for $R \geq 6$ a.u. The representation of MO can be improved by inclusion of united-atom $3d$ orbitals ($4f\sigma$ and $5g\sigma$ are then represented to better than 95% for all R). For a comment on how much an improved representation of MO alters the results of the 35-AO calculation, see below.

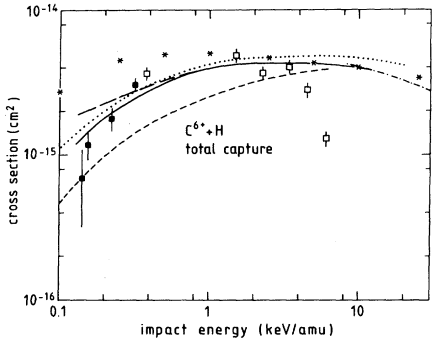

FIG. 2. Total electron transfer cross section in $C^{6+}+H$ collisions. Theoretical results: AO expansion with curved-line (solid line) and with straight-line (long-dashed line) internuclear trajectories, this work; 33-state MO expansion (Ref. 3) (dotted line); 10-state MO expansion (Ref. 6) (short-dashed line); numerical integration of the Schrödinger equation (Ref. 22) (dashed-dotted line); UDWA approximation (Ref. 12) (asterisks). Experimental results are by Phaneuf *et al.* (Ref. 24) (full squares) and by Panov *et al.* (Ref. 23) (open squares).

Figure 2 displays total transfer cross sections calculated in a range of impact energies with the 35-AO expansion and with the two choices of trajectories. At energies above 2 keV/amu, the AO results are very close to the other theoretical cross sections calculated with MO expansions,[3,6] the numerical integration[22] of the time-dependent Schrödinger equation, or with the UDWA approxima-

TABLE I. Cross sections (in 10^{-15} cm^2) for electron transfer into C^{5+} subshells (σ_n) and into all states (σ_{tot}) in $C^{6+}+H$ collisions. For each n, P_l denotes the normalized l-shell contribution.

E (keV/amu)	n	σ_n	P_0	P_1	P_2	P_3	P_4	σ_{tot}
0.133	4	1.17	0.10	0.21	0.22	0.47		1.21
	5	0.04						
0.2	4	1.76	0.06	0.18	0.27	0.49		1.82
	5	0.06						
0.318	4	2.28	0.08	0.16	0.30	0.47		2.39
	5	0.11	0.08	0.17	0.23	0.28	0.24	
0.637	4	3.27	0.08	0.20	0.37	0.35		3.47
	5	0.20	0.10	0.22	0.36	0.21	0.12	
1.0	4	3.67	0.07	0.22	0.38	0.33		3.93
	5	0.26	0.07	0.18	0.30	0.33	0.12	
2.25	4	3.90	0.06	0.22	0.38	0.34		4.30
	5	0.40	0.03	0.10	0.17	0.36	0.34	
4.0	4	3.88	0.05	0.20	0.38	0.37		4.32
	5	0.44	0.02	0.07	0.13	0.32	0.45	
6.25	4	3.50	0.04	0.17	0.37	0.42		4.32
	5	0.82	0.02	0.07	0.12	0.30	0.49	
12.25	4	2.78	0.03	0.15	0.35	0.47		3.87
	5	1.09	0.02	0.05	0.13	0.25	0.55	
25.0	4	1.92	0.02	0.10	0.23	0.65		2.76
	5	0.85	0.02	0.05	0.15	0.27	0.51	

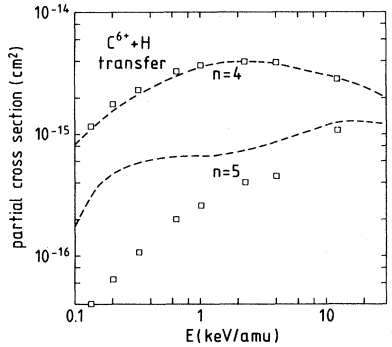

FIG. 3. Partial cross sections for transfer into C^{5+} $n=4$ and 5 orbitals in $C^{6+}+H$ collisions. Results of the present AO study are indicated by open squares, results of the 33-state MO investigation (Ref. 3) by dashed lines.

tion,[12] while experimental data by Panov *et al.*[23] fall off faster than all of these results with increasing energy. At energies below 2 keV/amu, the AO results calculated with a Coulomb trajectory are close to the MO results[3] of Green *et al.* and, overall, in harmony with the experimental data of Phaneuf *et al.*[24] and those of Panov *et al.*[23] There the MO calculation[6] by Vaaben and Briggs is too low by about a factor of 2, whereas the UDWA cross sections are too large. For clarity of presentation in Fig. 2, the results of the MO calculation by Salop and Olson without regard of translational factors are not included; they are, for the chosen origin at the target atom, close to the results of the extended MO expansion[3] and of the AO expansion calculations. The AO results calculated with a straight-line trajectory lie above those from a curved-line calculation, as discussed before.

Table I contains partial and total transfer cross sections for the 35-AO expansion calculation and the Coulomb internuclear trajectory. As expected, capture into $n=4$ orbitals is the dominant process with, however, capture into $n=5$ orbitals catching up at higher energies. The partial cross sections for capture into $n=4$ orbitals closely agree with the calculations by Green *et al.*[3] This is illustrated in Fig. 3 for the $n=4,5$ shell partial cross sections, and in Fig. 4 for the relative l ($n=4$) subshell cross-section fractions $P_l=\sigma_l/\sum_l\sigma_l$. In the l ($n=4$) distribution of transfer cross sections, Fig. 4, only at the high-energy end

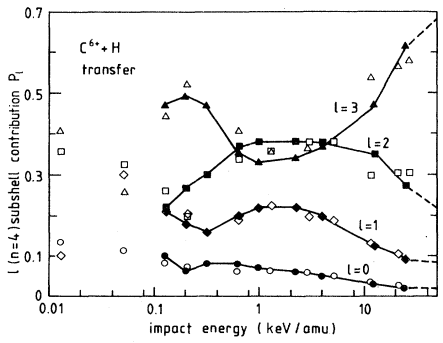

FIG. 4. Contribution of individual l subshells to electron transfer into the C^{5+} $n=4$ shell in $C^{6+}+H$ collisions. Solid symbols, linked by lines, designate results of the present study; open symbols those of the 33-state MO investigation (Ref. 3).

of the calculations where the MO picture is less applicable is there any notable disagreement between the two investigations based on AO and on MO expansions. There, the AO results at 25 keV/amu have been linked (by broken lines) to the results derived at 50 keV/amu from the classical-trajectory Monte-Carlo method,[25] displaying good harmony between the results from the two methods. The good agreement in Fig. 4 is, however, not necessarily indicative of good convergence of either of the calculations at small internuclear separations. There is evidence that the l distribution in the dominantly populated n shell is largely decided by the Stark effect at large separations.[26] Indeed, the l distribution from a merely three-state close-coupling calculation with subsequent consideration of Stark states gives[26] final l fractions close to those in Fig. 4.

For the $n=5$ partial cross sections, Fig. 3 reveals considerable discrepancies between the results from the AO and those from the MO expansion calculations, which increase with decreasing energies. Particularly, the low-energy shoulder in the results from the MO calculation is not seen in the AO results. It is not precisely clear what the reason for this discrepancy is. Of course, assuming the formation of MO in close collisions below 1 keV/amu is well founded, and it is not claimed that the particular AO basis set used leads to converged low-energy AO $n=5$ cross sections here. In test calculations with various modified AO basis sets, however, including some explicitly containing molecular binding effects through the presence of $5g$ or $3d$ united-atom orbitals, the low-energy $n=5$ partial cross sections were found to be different from those displayed in Fig. 3 and Table I by up to some 50%, a margin not surprisingly large given the smallness of the $n=5$ contribution against the dominant $n=4$ transfer at low energies. We note here that a similar peculiar disagreement is observed in the comparison of non-dominant partial cross sections for the case of low-energy $O^{8+}+H$ collisions, between the AO expansion calculations and the MO calculations. Further comments on this finding are, therefore, postponed to the end of this section.

B. $He^{2+}+H$

Electron transfer in $He^{2+}+H$ collisions has been investigated already with a number of methods in the past. Among those involving many-state expansions we mention here only the MO calculation by Hatton *et al.*,[27] the Sturmian expansion calculation by Winter,[28] the Hylleraas expansion calculation by Lüdde and Dreizler,[10] and the AO expansion calculations by Bransden and Noble[29] and by Fujiwara[30] (see references therein, too). As for total transfer cross sections, there is good agreement between all of these model calculations among each other and to experiment.[31] There is, however, some disagreement between measured and calculated partial cross sections for transfer into the $2s$ He^+ orbital at energies close to the cross-section maximum. We have, therefore, studied this partial transfer channel at one energy point, 5 keV/amu.

Calculations have been done with two AO+ basis sets. Both sets A and B include $1s$ H and $2s,2p,3d$ Li^{2+} (UA) orbitals at the H center. The He centered orbitals are, for

set A, the $n=1,2,3$ He^+ and $2s,2p,3d$ Li^{2+} orbitals and, for set B, the $n=1,2,3$ He^+ orbitals plus 18 psuedostates designed[32,33] to represent the He^+ continuum in a discretized way. At 5 keV/amu, partial $2s$ transfer cross sections from calculations with set A and B are, respectively, 2.25×10^{-16} and 2.18×10^{-16} cm^2, i.e., figures close to the results from the conventional AO expansion method[30] and other descriptions but distinctively larger than the experimental data[31] of 1.57×10^{-16} cm^2 (interpolated, 17% estimated absolute accuracy). It appears, therefore, that neither the inclusion of molecular binding effects (set A) in an AO expansion description nor that of continuum channels (set B) can explain this longstanding discrepancy between theories and experiment here. This conclusion is consistent with the results of a very recent investigation[34] undertaken by Bransden *et al.* on the basis of atomic-orbital expansions including pseudostates. Bransden *et al.* find[34] that, with a choice of 19 orbitals, calculated partial transfer cross sections into He^+ $n=2$ states are only little changed from the results of the related earlier study[29] based on a conventional AO expansion description.

C. $Be^{4+}+H$

From the discussion by Harel and Salin[5] it is known that, at low energies, electron transfer in $Be^{4+}+H$ collisions is effected mainly by couplings between, on one hand, the $4f\sigma$ MO (correlating to $1s$ H), and on the other hand, the $3d\sigma$ MO at about $R\simeq7$ a.u. as well as other MO correlating to $n=3$ UA for $R=0$ and to $n=3$ Be^{3+} for $R\to\infty$. Therefore, in the present study we have chosen, for low energies $E\leq2$ keV/amu, a 21-AO+ basis set consisting of the $n=2,3$ Be^{3+} and the $1s$ H orbitals as well as, at the Be center, the $4f$ UA orbitals and, at the H center, the $3d$ and $4f$ UA orbitals. The $3d$ UA orbitals have not been included at the Be center because they strongly overlap with the $3d$ Be^{3+} orbitals (which are included). For $E\geq2$ keV/amu where molecular effects are expected to be less important, calculations have been done with a conventional 20-AO basis set consisting of all $n=2,3,4$ Be^{3+} orbitals and the $1s$ H orbital.

Figure 5 shows calculated total capture cross sections over impact energy. At energies above 4 keV/amu, the present results are very close to those calculated in the UDWA approximation[12] and to those calculated[10] with an expansion into many Hylleraas functions. At lower energies, the present results fall considerably below the predictions in Ref. 12 and are fairly close to those from the 3-MO calculation.[5] The cross sections derived recently[9] on the basis of six traveling MO are considerably below the results of the present work. While that MO study[9] should lead to better converged cross sections than the simpler version[5] which neglects translational factors, the deviation from the results of this work may be related to the comment made in Ref. 9 that certain important couplings may still be missing. For example, in Ref. 9, rotational coupling is not included within the *full m* manifolds of $3dm$ or $3pm$ molecular orbitals, and this lack of consistent rotational coupling has already been found earlier[18] to be the source of underestimating transfer cross sections. Results of a study[35] with up to 10 nontraveling MO (not shown in Fig. 5) are much closer to the corresponding AO curve (calculated with straight-line trajectories), essentially coinciding with the latter at 0.25 keV/amu and overestimating the latter by at most 15% at energies as high as 12.25 keV/amu. These results appear[35] to have converged against an enlargement of the MO basis. Surprisingly, in calculations with smaller basis sets almost identical to the one used in Ref. 9 but without translational factors, total transfer cross sections are little changed from those of the largest MO basis set. For the present case, therefore, it seems that a MO calculation without translational factors gives better-converged results than a closely related MO calculation including translational factors, be it by mere coincidence or by a numerical problem in either of the MO calculations.

At about 0.2 keV/amu, a small peak structure is seen in the total capture cross section calculated with the AO+ expansion and a straight-line internuclear trajectory. This structure is likely to be an artifact of the present model and indicative of the decreasing convergence of the results at the lowest energies in Fig. 5. Since, at low energies, the impact-parameter-dependent transition probabilities from the calculations oscillate strongly and are certainly not converged within the limited calculation, we did not further investigate the precise reason for the structure in the low-energy total capture.

In Table II, calculated total and partial capture cross sections are listed at selected impact energies. Results are given from calculations employing the Coulomb internuclear trajectory. (Note that, in the AO+ results, $E\leq2$ keV/amu, the total transfer cross sections σ_{tot} contain small contributions from capture into the $4f$ UA orbitals which strongly overlap with $4f$ Be^{3+} orbitals.) Capture into $n=3$ Be^{3+} orbitals dominates over all other channels at all energies, though to a lesser degree at the highest energy. The broad shape of the cross-section maximum suggests the presence of important couplings between more than merely two σ orbitals. For example, rotational coupling between the initial $4f\sigma$ MO and the $3d\pi$ MO at fin-

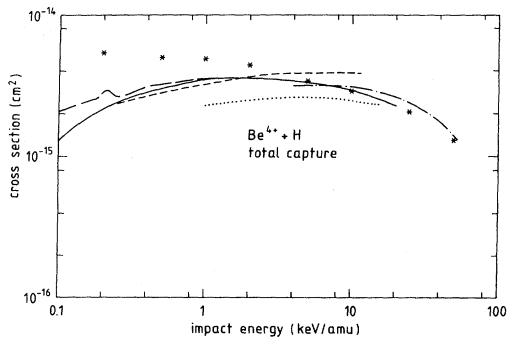

FIG. 5. Total electron transfer cross sections in $Be^{4+}+H$ collisions. Solid and long-dashed lines designate results of the present study with, respectively, curved-line and straight-line trajectories. Other theoretical results: three-state MO expansion (Ref. 5) (short-dashed line); six-state MO expansion (Ref. 9) (dotted line); Hylleraas expansion (Ref. 10) (dashed-dotted line); UDWA approximation (asterisks).

TABLE II. Cross sections (in 10^{-15} cm^2) for electron transfer in $Be^{4+}+H$ collisions.

E (kev/amu)	n	σ_n	P_0	P_1	P_2	P_3	σ_{tot}
0.1	2	0.04	0.47	0.53			1.28
	3	1.22	0.16	0.38	0.46		
0.2	2	0.04	0.44	0.56			2.13
	3	2.01	0.13	0.28	0.59		
0.5	2	0.05	0.44	0.56			2.98
	3	2.80	0.11	0.28	0.61		
1.0	2	0.06	0.40	0.60			3.49
	3	3.23	0.10	0.31	0.60		
2.0	2	0.04	0.23	0.77			3.47
	3	3.23	0.09	0.33	0.59		
2.0[a]	2	0.08	0.49	0.51			3.68
	3	3.31	0.10	0.37	0.53		
	4	0.29	0.09	0.24	0.42	0.26	
5.0	2	0.08	0.25	0.75			3.32
	3	2.93	0.08	0.37	0.55		
	4	0.31	0.04	0.14	0.41	0.41	
10.0	2	0.05	0.34	0.66			2.94
	3	2.45	0.05	0.31	0.63		
	4	0.45	0.03	0.09	0.30	0.58	
20.0	2	0.10	0.37	0.63			2.28
	3	1.73	0.34	0.22	0.75		
	4	0.46	0.04	0.11	0.31	0.54	

[a]Results above this line are calculated with a 21-AO+ expansion, those on and below this line with a 20-AO expansion; see text.

ite internuclear separations probably plays a major role.[5] The results from the 21-AO+ calculation and those from the 20-AO calculation agree reasonably well at 2 keV/amu where the transition between the two choices of basis sets is done. Slight discrepancies between the two sets of results at 2 keV/amu indicate the degree of accuracy of the calculations.

D. $B^{5+}+H$

In a simplified consideration of the slowly colliding system $B^{5+}+H$, the incoming electron, starting from its initial $1s$ H configuration, develops[5] along the $5g\sigma$ MO which strongly couples with the $4f\sigma$ MO at internuclear separation $R\simeq 13$ a.u. From the $4f\sigma$ MO, the electron

TABLE III. Cross sections (in 10^{-15} cm^2) for electron transfer in $B^{5+}+H$ collisions.

E (keV/amu)	n	σ_n	P_0	P_1	P_2	P_3	P_4	σ_{tot}
0.1	3	0.16	0.29	0.39	0.32			1.21
	4	1.05	0.15	0.35	0.34	0.17		
0.2	3	0.30	0.17	0.36	0.47			1.26
	4	0.95	0.11	0.30	0.35	0.24		
	5	0.01						
0.5	3	0.37	0.23	0.42	0.35			1.58
	4	1.14	0.08	0.22	0.34	0.36		
	5	0.06						
1.0	3	0.30	0.23	0.39	0.38			2.14
	4	1.69	0.06	0.19	0.31	0.43		
	5	0.14	0.07	0.20	0.32	0.25	0.16	
2.0	3	0.46	0.20	0.30	0.50			2.49
	4	1.90	0.05	0.17	0.35	0.43		
	5	0.13	0.09	0.16	0.20	0.25	0.31	
5.0	3	0.75	0.20	0.46	0.34			3.05
	4	2.14	0.03	0.14	0.33	0.50		
	5	0.16	0.06	0.12	0.17	0.26	0.39	
10.0	3	0.80	0.12	0.42	0.46			3.33
	4	2.35	0.03	0.08	0.28	0.61		
	5	0.19	0.03	0.09	0.16	0.23	0.49	
20.0	3	0.86	0.08	0.35	0.56			2.90
	4	1.73	0.02	0.07	0.21	0.70		
	5	0.31	0.03	0.09	0.19	0.35	0.34	

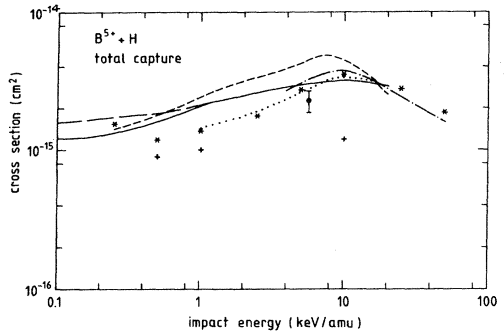

FIG. 6. Total electron transfer cross sections in $B^{5+}+H$ collisions. For an explanation of symbols, see caption to Fig. 5, except for the crosses which designate results of the multichannel Landau-Zener study (Ref. 11) and one experimental point (Ref. 36) (full circle).

may be moved, probably under the influence of further couplings, finally into the $n=4$ B^{4+} orbitals, or may, though a lesser degree,[5] be further transferred into the $n=3$ B^{4+} orbitals by virtue of a $4f\sigma$-$3d\sigma$ coupling at $R\simeq 5$ a.u.

In this study, electron transfer in $B^{5+}+H$ collisions has been calculated mainly with a 41-AO+ basis set consisting, at the B center, of the $n=3,4,5$ B^{4+} orbitals and, at the H center, of the $n=1$ H and the $4f$, $5g$ UA orbitals. In test calculations without UA orbitals, i.e., with a 32-AO basis set, the total and the $n=4$ partial cross sections turned out to be little changed from the 41-AO+ results, with deviations amounting to about 10%. Only the partial cross sections for transfer into $n=3$ orbitals displayed a major sensitivity to the presence of UA orbitals, with deviations of up to 50% between the 41-AO+ and the 32-AO results. For energies below 1 keV/amu, instead of the $n=5$ B^{4+} orbitals, the $5g$ UA orbitals are included at the B center.

In Table III, calculated total and partial transfer cross sections in $B^{5+}+H$ collisions are given. Although capture into $n=4$ orbitals dominates over the $n=3$ and 5 channels at all energies, the capture process is less selective than in the $Be^{4+}+H$ case. Here, capture into $n=3$ orbitals still contributes to roughly 25% of the total capture cross section over the energy range considered.

The large number of couplings effective in this system render it an intriguing target for theoretical investigations. In Fig. 6, calculated total capture cross sections are depicted over impact energy. The deviations between results from the present study and from the 3-MO study[5] and the Hylleraas expansion calculation[10] are larger than those observed in the $Be^{4+}+H$ case. Deviations between the cross sections of the improved MO study[9] and those of the present work are of the same order as in the case of $Be^{4+}+H$ collisions, and the comments made there on this point apply here, too. Cross sections calculated with the UDWA method[12] are also given in Fig. 6, and are, again, seen to be reliable only at higher energies. Cross sections from the multichannel Landau-Zener method[11] are distinctively lower than those from the other descriptions and contain the $n=3$ partial cross sections as dominant contributions with only small admixtures of $n=4$ cross sections, in contrast to the present results, cf. Table III. There is only one experimental point[36] at 5.6 keV/amu. It is in fair accord with all of the recent theoretical results, except the results from the application of the Landau-Zener method.

E. $N^{7+}+H$

Of all the collision systems under consideration in this work, the system $N^{7+}+H$ is the one which has been least investigated in the past. Since the molecular energy diagram is not easily accessible in the literature, its main part is shown in Fig. 7. Of course, the structure of this diagram is very much alike that for $C^{6+}+H$, cf. Fig. 1, if orbitals are relabeled.

Disregarding quasidiabatic transitions between the initially populated MO and other higher-lying MO at large internuclear separations R, Fig. 7 shows that, in slow $N^{7+}+H$ collisions, the electron moves into the collision zone on the $6h\sigma$ orbital. At separations $R\simeq 12$ a.u., strong couplings with the $5g\sigma$ MO may act as the doorway to transfer into $n=5$ orbitals, while, depending on the diabaticity of this strong coupling, further couplings between the $5s\sigma,\ldots,5f\sigma$ and either the $5g\sigma$ or the $6h\sigma$ may play an important role. Couplings between the $5g\sigma$ MO and the $4f\sigma$ MO (not shown in Fig. 7) at $R\simeq 5$ a.u. may lead to the moderately strong population of $n=4$ N^{6+} orbitals. Therefore, AO expansion calculations for $N^{7+}+H$ collisions have been done with a basis of those atomic orbitals to which the aforementioned MO correlate at large separations, plus those which might be populated by couplings of the $6h\sigma$ MO to higher MO at small separations. That is, the basis set consists of the $1s$ H orbital at the target center and all $n=4,5,6$ N^{6+} orbitals at the projectile center, with the exception of the $6s$ orbital which is omitted.

Figure 8 shows the calculated total transfer cross sections of the AO expansion calculations with curved-line and with straight-line internuclear trajectories. They display a similar trend of peaking at small impact energies as displayed by the results of a Landau-Zener study[37] based on the two major radial couplings mentioned above, and by the results of the recent multichannel Landau-Zener study.[11] Apparently, the reason[37] for the low-

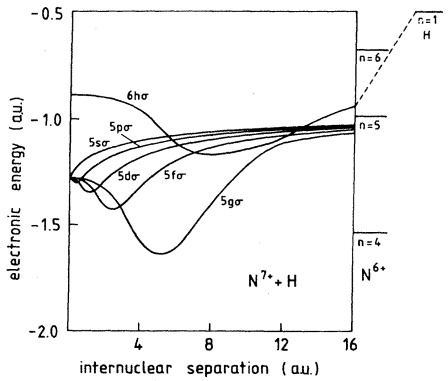

FIG. 7. Molecular energy diagram of σ states in the $N^{7+}+H$ system.

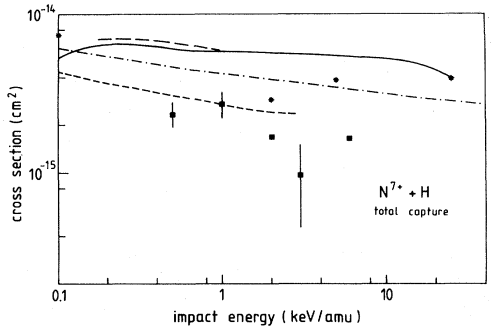

FIG. 8. Total electron transfer cross sections in $N^{7+}+H$ collisions. Results of this study are shown as solid and as long-dashed lines for, respectively, curved-line and straight-line trajectories. Other theoretical results: multichannel Landau-Zener study (Ref. 11) (dashed-dotted line); two-state Landau-Zener study (Ref. 37) (dashed line); UDWA approximation (Ref. 38); (asterisks). Experimental data (Ref. 23) (solid squares) are by Panov *et al.*

energy position of the cross-section maximum in the Landau-Zener studies, i.e., the narrowness of the avoided coupling at separations $R \simeq 12$ a.u., gives rise to the shape in the AO expansion calculation too. The discrepancies of the magnitudes of cross sections, however, between, on one side, results in this work and in the multichannel Landau-Zener study,[11] and, on the other side, in the simpler earlier Landau-Zener study[37] indicate the importance of rotational couplings and possibly other radial couplings in a consistent study within a molecular basis. The remaining deviations between results from the improved Landau-Zener study[11] and from the present work are of the same order as observed[11] for $C^{6+}+H$ and $O^{8+}+H$ collision systems and, hence, can be considered typical for uncertainties in the Landau-Zener approximation to close-coupling situations in the currently considered range of energies and of atomic charge numbers Z. At higher energies, the current calculated transfer cross sections join in smoothly with those from the UDWA investigation.[38] The cross sections measured[23] by Panov *et al.* are consistent with the predictions of the earlier Landau-Zener description[37] and, hence, far below the AO cross sections. With consideration of their large error bars, however, and of similar discrepancies for the other collision systems ($C^{6+}+H$, $O^{8+}+H$), it seems that these measurements cannot be taken as an ultimate test of theories yet. The current calculated total and partial transfer cross sections are listed in Table IV. As suggested by the molecular energy diagram, $n=5$ orbitals are predominantly populated, with the contributions of $n=4$ and $n=6$ transfer becoming larger as the energy increases. As in the case of $B^{5+}+H$ collisions, the Landau-Zener study leads to partial cross sections σ_n with much stronger population of small-n orbitals than seen in the present work. For example, at 1 keV/amu, σ_5/σ_4 is about 1.3 in the Landau-Zener work[11] but 4.6 in the present study, illustrating the limited accuracy of partial cross sections from the Landau-Zener study as n approaches the charge number Z.[11]

TABLE IV. Cross sections (in 10^{-15} cm^2) for electron transfer in $N^{7+}+H$ collisions.

E (keV/amu)	n	σ_n	P_0	P_1	P_2	P_3	P_4	P_5	σ_{tot}
0.1	4	0.17	0.16	0.13	0.31	0.40			5.25
	5	5.04	0.13	0.29	0.28	0.20	0.10		
	6	0.04							
0.2	4	0.42	0.14	0.17	0.26	0.43			6.54
	5	6.03	0.10	0.22	0.23	0.24	0.21		
	6	0.09							
0.3	4	0.41	0.11	0.23	0.29	0.37			6.47
	5	5.93	0.06	0.15	0.21	0.27	0.31		
	6	0.13		0.10	0.17	0.29	0.27	0.17	
0.6	4	0.65	0.09	0.21	0.37	0.33			5.94
	5	5.09	0.05	0.13	0.20	0.25	0.37		
	6	0.20		0.13	0.22	0.24	0.26	0.15	
1.0	4	1.02	0.09	0.25	0.36	0.30			5.94
	5	4.72	0.04	0.12	0.20	0.28	0.36		
	6	0.20		0.13	0.17	0.26	0.28	0.16	
2.0	4	1.52	0.09	0.23	0.33	0.32			5.71
	5	3.94	0.03	0.10	0.19	0.32	0.36		
	6	0.25		0.05	0.14	0.15	0.30	0.35	
4.0	4	1.88	0.09	0.26	0.27	0.38			5.51
	5	3.39	0.02	0.08	0.19	0.34	0.36		
	6	0.24		0.04	0.09	0.13	0.25	0.50	
10.0	4	1.55	0.06	0.21	0.35	0.38			5.26
	5	3.33	0.01	0.06	0.15	0.31	0.48		
	6	0.38		0.03	0.09	0.17	0.26	0.45	
25.0	4	1.40	0.04	0.15	0.34	0.47			3.86
	5	1.88	0.01	0.05	0.12	0.26	0.56		
	6	0.58		0.05	0.11	0.17	0.23	0.44	

F. $O^{8+}+H$

The electron transfer mechanism in $O^{8+}+H$ collisions has been discussed previously by Harel and Salin[5] and by Salop and Olson,[8] and has been thoroughly investigated by Shipsey *et al.*[4] From these works transfer is known to occur predominantly into the O^{7+} $n=5$ shell and to be initiated, in low-energy collisions, mainly by $6h\sigma$-$5g\sigma$ radial couplings. In the present investigation we have adopted an AO basis set analogous to that used by Shipsey *et al.* While the latter used sets containing all MO which correlate to O^{7+} $n=4,5,6$ and H $1s$ states, in the present work all these atomic orbitals have been included with the exception of the $6s$ O^{7+} orbital. Orbitals with $n\geq 7$ were not included in the AO basis set although a few of the MO used in the MO basis correlate to O^{7+} $n\geq 7$ orbitals. While the MO calculations has been broken up into three separate calculations (employing 33 MO each) for reasons of reducing the computational effort, in the present investigation the full 46-AO basis set has been used in a single consistent calculation for all the partial transfer cross sections and the total transfer cross section.

Calculated partial and total transfer cross sections are given in Table V. The total cross sections are displayed and compared to results from the literature in Fig. 9. The total transfer cross section from the 46-AO calculation is very close to those from the extended MO calculations[4] at energies above 1 keV/amu. With decreasing energies below that energy, the cross sections from the AO expansion calculation, using a curved-line trajectory, fall increasingly below the MO results, while the use of a straight-line trajectory leads to cross sections close to those from the MO calculation. The results from the eight-state MO calculation,[8] without translational factors and with two choices of origin, is in qualitative harmony with the extended MO calculation[4] while the three-state MO study[5] is clearly not sufficient here. The comparatively good agreement of the UDWA calculation[12] with both large-scale MO and AO calculations over the full energy range seems to be fortuitious. The experimental results by Panov *et al.*[23] are well below the best theoretical descriptions.

The comparison between partial cross sections for transfer into individual O^{7+} n shells in $O^{8+}+H$ in Fig. 10 shows why, in the total transfer cross sections for the present system, the MO calculation (using an averaging procedure for the internuclear trajectory) seems to be in better agreement with the AO expansion calculation using a straight-line trajectory and not, as is the case for $C^{6+}+H$ collisions, with that using a Coulomb trajectory. As is seen in Fig. 10, the dominant partial cross sections for transfer into $n=5$ orbitals from the present calculation employing the Coulomb trajectory are in fact very close to the corresponding results from the MO calculation. However, there is some disagreement in the $n=6$ partial cross sections at low energies which, in the present calculation, constitute only a small contribution to the total transfer cross section but a large one in the MO calculation. Surprisingly, they become even larger than the $n=5$ partial cross section below 0.1 keV/amu in the MO calculation.[4] There is also sizable disagreement in the

TABLE V. Cross sections (in 10^{-15} cm^2) for electron transfer in $O^{8+}+H$ collisions.

E (keV/amu)	n	σ_n	P_0	P_1	P_2	P_3	P_4	P_5	σ_{tot}
0.1	5	1.00	0.03	0.14	0.19	0.26	0.39		1.03
	6	0.03		0.16	0.20	0.21	0.26	0.17	
0.202	4	0.02	0.14	0.17	0.26	0.43			2.58
	5	2.37	0.06	0.15	0.19	0.22	0.37		
	6	0.19		0.17	0.23	0.23	0.23	0.13	
0.4	4	0.07	0.05	0.19	0.27	0.49			3.68
	5	3.23	0.06	0.14	0.18	0.29	0.33		
	6	0.37		0.15	0.22	0.29	0.19	0.15	
1.0	4	0.20	0.11	0.27	0.26	0.36			5.48
	5	4.60	0.04	0.14	0.26	0.31	0.25		
	6	0.68		0.11	0.18	0.22	0.28	0.21	
2.0	4	0.56	0.11	0.29	0.32	0.27			6.05
	5	4.47	0.04	0.14	0.26	0.29	0.26		
	6	1.02		0.04	0.11	0.16	0.32	0.36	
5.0	4	0.47	0.09	0.22	0.33	0.37			6.20
	5	4.57	0.03	0.11	0.23	0.36	0.27		
	6	1.16		0.03	0.08	0.15	0.27	0.47	
10.0	4	0.46	0.07	0.27	0.34	0.31			5.85
	5	4.35	0.02	0.08	0.19	0.32	0.39		
	6	1.50		0.03	0.07	0.16	0.29	0.46	
20.0	4	0.69	0.07	0.22	0.36	0.35			4.71
	5	2.84	0.01	0.06	0.16	0.33	0.43		
	6	1.17		0.03	0.09	0.15	0.26	0.47	
30.0	4	0.78	0.05	0.19	0.35	0.41			3.75
	5	1.95	0.01	0.05	0.13	0.31	0.50		
	6	1.02		0.04	0.08	0.15	0.21	0.52	

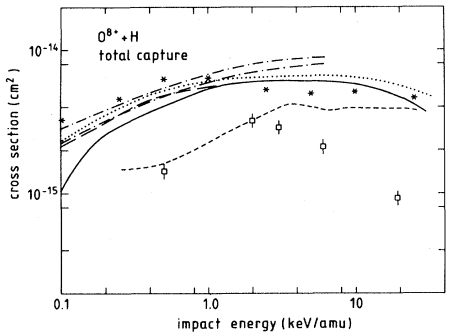

FIG. 9. Total electron transfer cross section in $O^{8+}+H$ collisions. Theoretical results: AO expansion with curved-line (solid line) and with straight-line (long-dashed line) internuclear trajectories, this work; multistate MO expansion (Ref. 4) (dotted line); eight-state MO expansion (Ref. 8) (dashed-dotted lines) with two choices of origin; three-state MO expansion (Ref. 5) (short-dashed line); UDWA approximation (Ref. 12) (asterisks). Open squares designate experimental results by Panov *et al.* (Ref. 23).

magnitude of the $n=4$ partial cross sections between the AO and MO calculations but these do not much influence the total transfer cross sections due to their overall smallness in both calculations. The AO partial cross sections at 30 keV/amu have been linked (by dashed lines) to results from the classical-trajectory Monte Carlo method at 50 keV/amu. It is seen that the results for $n=5$ and 6 from both methods are consistent with each other while the structure of the $n=4$ partial cross section does not allow a definite conclusion.

From the material at hand, it is hard to assess the reason for the large discrepancies between low-energy $n=6$ partial cross sections from the MO work and from the present one. Physically, an enhancement in the $n=6$ cross section might be expected at very low energies due to transitions at a $6h\sigma$-$7i\sigma$ narrowly avoided crossing (at $R\approx 16.7$ a.u.).[4] This enhancement would be observed in both AO and MO expansion calculations which, at such large internuclear separations, are virtually equivalent. However, Shipsey *et al.* note[4] that the large $n=6$ cross sections observed in their MO work are due mainly to $6h\sigma$-$6h\pi$ rotational coupling. Again, at large internuclear separations R where the larger part of transfer cross sections are accumulated, this mechanism is included in the present study through the presence of O^{7+} $6hm$ ($m=0$–5) atomic orbitals, while at smaller R it is at least accounted for to a fair approximation. To us it seems unlikely that the disagreement in question should be prompted by different choices of translational factors between the two descriptions, by different trajectories or by the neglect[4] of certain couplings in the MO work. At any rate, the presence of an as yet unresolved numerical problem in either of the calculations cannot be completely excluded at this point. Further theoretical and experimental information is needed to explore these inconsistencies.

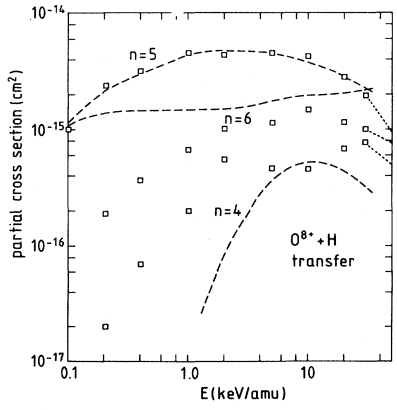

FIG. 10. Partial cross sections for transfer into O^{7+} $n=4$, 5, and 6 orbitals in $O^{8+}+H$ collisions. Results of the present AO study are indicated by open squares, results of the multistate MO investigation (Ref. 4) by dashed lines.

IV. CONCLUDING REMARKS

In this work atomic-orbital expansions have been employed in calculations of total and partial transfer cross sections for one-electron collision systems $He^{2+}+H$, $Be^{4+}+H,\ldots,O^{8+}+H$ in the energy range 0.1–30 keV/amu. For the collision systems $He^{2+}+H,\ldots,$ $B^{5+}+H$, some united-atom orbitals have been included as pseudostates in the expansion in order to simulate the influence of molecular binding effects in slow collisions. For the $He^{2+}+H$ system, additional pseudostates have been used in order to simulate the effect of ionization channels. For $C^{6+}+H,\ldots,O^{8+}+H$, conventional atomic-orbital basis sets have been used in the main calculations.

With regard to the internuclear trajectory in the semiclassical approximation, two points are made here.

(a) The transfer cross sections are found to depend on the internuclear trajectory in collisions below an energy of 1 keV/amu. The degree of this dependence varies according to the varying contribution of small-impact-parameter collisions to transfer cross sections in these systems. For example, in $C^{6+}+H$ collisions at 0.1 keV/amu, the calculations with a straight-line trajectory gives cross sections about twice as large as does an unscreened Coulomb trajectory, while for the $B^{5+}+H$ system this enhancement factor is only 1.3. This finding is in qualitative agreement with results derived with the MO expansion[9] of Kimura and Thorson. With that expansion, for the $B^{5+}+H$ system at 0.1 keV/amu, the total transfer cross section calculated with a straight-line trajectory is a factor of 1.2 above the results derived with an unscreened Coulomb trajectory.[39] However, in a model study for the $C^{6+}+H$ system, Green *et al.* report[40] much smaller trajectory effects than observed in the present work. For example, at 0.21 keV/amu, the enhancement factor of the straight-line trajectory calculation is only 1.13, and at 0.05 keV/amu, the straight-line trajectory calculation gives even *smaller* cross sections than does the Coulomb trajectory.[40] No reason for this apparent discrepancy with the present work can be given here. Through communication with Green and Riley it has been established that the distribution of transfer probabilities over impact parameters is roughly the same in both AO and MO methods, ruling out the most obvious possible reason for different trajectory effects between the two methods. A direct comparison of

transfer probabilities is hampered by their strongly oscillating structures whose calculated details almost certainly have no physical significance although the structures themselves are real.

(b) In the cases of $C^{6+}+H$ and $O^{8+}+H$ collisions where detailed molecular-orbital expansion calculations, using an averaged trajectory method, are available,[3,4] the AO expansion calculations with a trajectory derived from an unscreened Coulomb potential give results close to those from the MO expansion, at least for the respective dominant partial cross sections. This is interpreted as an indication that Coulomb trajectories are very much appropriate for the systems under consideration. This is confirmed in an investigation[41] of transfer cross sections for $C^{4+}+H$ collisions which, at some 0.1 keV/amu, join smoothly with a full quantum mechanical MO expansion calculation at lower energies if, in the AO+ expansion calculation,[41] a Coulomb trajectory is assumed. It is, however, again at variance with the conclusions from the model study[40] by Green *et al.* who find the straight-line trajectory to give results closer to those from alternative, physically sounder methods.

It is, therefore, admitted that the role of trajectory effects in charge transfer studies below 1 keV/amu is still not unambiguously explored, and no solution for this problem is offered here. Further theoretical work may help to clarify the present situation marked by as yet inconsistent conclusions from works by various groups. It is, moreover, expected that future, sufficiently precise measurements at low energies will provide valuable guidance here.

The calculated partial cross sections have been compared to results from the extended MO calculations,[3,4] for $C^{6+}+H$ and $O^{8+}+H$ collisions. The partial cross sections for transitions into the respective dominant n shells ($n=4$ or 5) are found to agree well over the whole energy range between the two studies. The same is true for the l subshell contributions, too, and this is explained in the studies by Salin *et al.*[26] based on an investigation of the Stark effect in these collisions. However, for the nondominant n shells, the calculated partial transfer cross sections agree only as they approach the highest energies considered here. At lower energies, they certainly need further theoretical and experimental exploration. It seems that such exploration can only be done within large-scale close-coupling schemes. The UDWA approximation to those schemes is apparently insufficient, at least at energies below 10 keV/amu if detailed results are required. Similarly, the Landau-Zener approximation even in its multichannel version gives only rough guidance for total transfer cross sections and, for some of the systems considered, partial cross sections with considerable bias towards contributions of small-n shells, when compared to results of close-coupling studies.

From the comparison of results for $C^{6+}+H$ and $O^{8+}+H$ collisions it is inferred that, also for the other collision systems, the current calculated total transfer cross sections are essentially converged, probably to some 10%, and so are the partial transfer cross sections for the dominant channels. Partial transfer cross sections for the nondominant channels are probably not as accurate. At lower energies, these small transitions would be particularly affected by an improved representation of molecular binding, i.e., by consistent inclusion of united-atom orbitals in the present model. At higher energies, the broadening of the n distribution is the main source of uncertainties, and this again affects mostly the small channels included in the present investigation. The broadening of the n distribution of transfer cross sections as well as continuum contributions are, of course, the main obstacles precluding extension of the present calculations to still higher energies.

As is well known, low-energy transfer cross sections for the various ${}_ZX^{Z+}+H$ collision systems do not obey any strict scaling rule since the particular molecular structure of a given system is too important. This is reflected in the markedly different shapes of total transfer cross sections for $Be^{4+}+H,\ldots,O^{8+}+H$ collisions when plotted over impact energy. Still, there is overall similarity between the shapes of cross-section bumps for $Be^{4+}+H$, $C^{6+}+H$, and $O^{8+}+H$ collisions, which are all characterized by a single maximum and by distinctively decreasing cross sections in the tails below some 1 keV/amu and above some 10 keV/amu. In a molecular picture, the similar structure is understood by a similar position R_n of the particular avoided crossing which initiates the population of the most prominent n channels by radial couplings. Namely, for these systems, the respective R_n are in a narrow range of some 7–9 a.u., i.e., in a range most favorable for radial electronic transitions at the considered energies. On the other hand, transfer cross sections for $B^{5+}+H$ and $N^{7+}+H$ collisions do not show a clear decay at lower energies in the considered energy range. This again is certainly related to the positions R_n of the corresponding avoided crossings, R_n being here in the range 12–13 a.u. At these crossings, transitions occur effectively only at lower energies, typically below some 1 keV/amu.[9] In turn, it is clear that, for the latter systems, transitions at higher energies occur via rotational couplings or other nonlocalized radial couplings so that a broader structure of cross sections emerges. The role of rotational couplings in $B^{5+}+H$ collisions has been stressed in the MO investigation[9] by Kimura and Thorson. It probably is the reason why the $B^{5+}+H$ and the $N^{7+}+H$ systems are less suitable targets for investigations within the Landau-Zener method.

In conclusion, we note that even with the largest basis sets employed in this study, i.e., those with 46 atomic orbitals extending up to the $n=6$ shells of the projectiles, numerical problems were not encountered. An extension of the present study to still larger basis sets or to moderately higher-Z projectiles seems, therefore, very feasible and should not pose additional problems other than increased computer time. This investigation is intended to provide a general and improved framework for discussing forthcoming experiments on the systems under investigation here, as well as for assessing the results of simpler models. With the availability of more precise experimental data, cross sections could also be readily calculated, with present-day facilities, to a higher precision too for selected collision systems at a choice of collision energies.

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