Molecular-state treatment of excitation and charge-transfer processes in $H^+ + He(1s^2)$ collisions

M. Kimura
Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80309

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The molecular-state expansion method within the impact-parameter formalism is applied to the processes $H^+ + He(1s^2) \rightarrow H(nl) + He^+(1s)$ and $H^+ + He(1s^2) \rightarrow H^+ + He(1s,2l)$. Electron translation factors are incorporated into the scattering wave function, so that the cross sections obtained are free from the origin dependency. It is shown that stepwise flux promotion is the primary mechanism for excitation and electron capture into excited states at lower energies, and hence it is necessary to include all these channels in the close-coupling method to achieve reliable results.

I. INTRODUCTION

The theoretical study of proton-helium inelastic scattering dates back to a paper by Massey and Smith[1] in the early 1930's. Since then, ample theoretical data[2–8] have been accumulated—particularly in the energy range above 10 keV. At lower energies, however, there exists no systematic investigation of the process, and hence the marked disagreement between the three sets of experiments[9–11] and the theoretical results[4–7] for the charge-transfer cross section has not been clarified. This implies that the application of a sophisticated molecular-state treatment is really necessary to study the system in the low-energy regime.

Apparently as the energy increases to the intermediate-energy region, the $He(2^1S)$ and $He(2^1P)$ excitation channels may play an important role in understanding the overall dynamics comprehensively. Thus, these excitation channels as well as the excited-state capture channels must be included in any theoretical calculation. Recently, solid measurements for the $He(2^1S)$ and $He(2^1P)$ excitation cross sections in the 25–100-keV energy region have become available.[12] These provide useful information for checking the validity of the various theoretical approaches. The aim of this report is to investigate systematically the charge transfer and excitation processes in the low- to intermediate-energy region, where the discrepancies among the theories and experiments are still unresolved.

II. THEORETICAL METHOD

The molecular-orbital (MO) expansion method [or the perturbed-stationary-state (PSS) method] is employed to study the dynamics of the proton-helium collision below the collision energy of 40 keV. Electron translation factors (ETF's) were properly incorporated into the molecular-state expansion,[13] and hence our calculated cross sections are independent of the origin chosen for the electron coordinate. This is unlike the other theoretical result[8] which also used a molecular treatment but neglected the ETF's. The resulting coupled equations (retaining the first-order term in $\mathbf{V}$) have been solved numerically for the transition amplitudes which are then used to calculate the cross sections. The magnitude of neglected higher-order coupling terms in $\mathbf{V}$ is roughly related to the size of the coupling. As we will discuss later, all the important couplings which play a role as an exit from the initial channel are short range. Therefore, the contribution of the higher-order terms in $\mathbf{V}$ to a calculation for the charge transfer to the $H(1s)$ state should be small in the energy range studied. However, couplings among Rydberg states are long range, and hence a neglect of higher-order terms may cause the overestimation to the calculated cross section for these channels above $v > 1$ a.u. The details of the theoretical treatment have already been explained elsewhere[13] and need not be reported here.

Full configuration-interaction (CI) calculations were performed to obtain eigenvalues and eigenfunctions of the electronic Hamiltonian. Slater-type orbitals (STO's) were employed as basis functions. Values of the orbital exponents for the STO's are listed in Table I.

Figure 1 shows the adiabatic potential curves of the HeH^+ system as a function of internuclear distance R. Note that only singlet states are needed in the present case.

The accuracies of our calculated energies are within 0.1

TABLE I. Orbital exponents of the STO basis functions.

He		H	
$1s$	4.346	$1s$	5.000
	2.780		2.000
	1.453		1.000
$2s$	5.30	$2s$	5.000
	3.40		1.000
	2.50		
$2p$	4.30	$2p$	5.000
	2.40		1.000
	1.50		

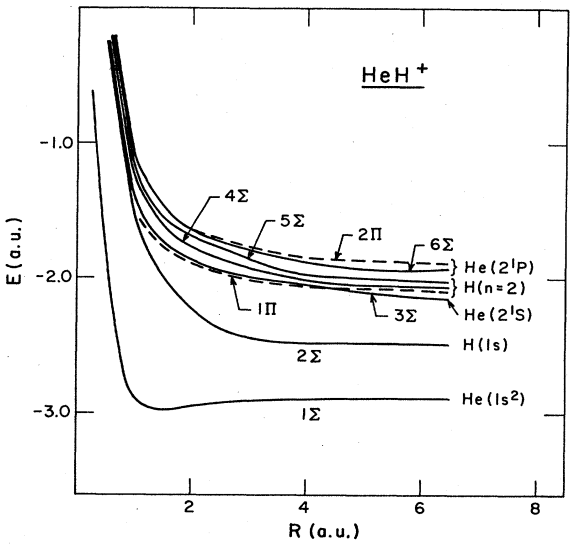

FIG. 1. Adiabatic potential curve for the HeH^+ system.

eV of the spectroscopic values for all the states considered. The constant energy gap between the initial and first charge-transfer channel gives rise to a typical Demkov coupling between these states and is expected to provide the first step of the dominant flux promotion into the 2Σ state. Indeed, the calculated radial coupling between 1Σ and 2Σ has a peak at $R \simeq 2.5$ a.u. and dies off at $R \simeq 6$ a.u. Also it might be worth noting that the $H(n=2)$ excitation levels are located energetically below the $He(2^1P)$ levels, so that qualitatively, at lower collision energies, the electron may be promoted to the $He(2^1P)$ excitation level by the stepwise promotion through each of the lower levels (ladder-climbing mechanism). In contrast, at higher collision energies, direct excitation may be the prevailing mechanism for $He(2^1P)$ excitation. As far as the nonadiabatic couplings are concerned, the important radial couplings, which connect to the 1Σ state, are all short range, i.e., they vanish for $R \lesssim 6$ a.u. This characteristic reflects the nature of the HeH^+ molecular structure, i.e., since the electrons in the He atom are bound very tightly, and the atomic core size is on the order of a half atomic unit, the atomic character of the system persists until the colliding partner approaches to a very close distance (say, $R \lesssim 2$ a.u.).

In general, the couplings among the higher levels display a sharp peak around $R \sim 5$ a.u. and a broad maximum in the outer region. This characteristic feature is apparently attributed to the presence of an avoided crossing at smaller R, followed by a Demkov coupling or Stark-mixing effect depending upon the states considered. The sharp peak in the couplings at small R plays an important role for the flux promotion to the higher levels, while the broad maximum in the outer region produces secondary effects. We have carried out an eight-state close-coupling calculation which includes the initial state $[H^+ + He(1s^2)]$, the charge-transfer states $[H(1s) + He^+(1s), H(n=2) + He^+(1s)]$, and the excitation states $[H^+ + He(2^1S), He(2^1P)]$.

The results for the calculated probabilities are compared with those of Green, Stanley, and Chiang[4] (GSC) who have adopted two-state atomic-orbital (AO) expansion methods. At 1 keV the magnitude of the peaks at small impact parameter ($\rho \lesssim 1.5$ a.u.) in their result is appreciably greater than the present results, although the overall structure is quite similar. This discrepancy obviously diminishes as the collision energy increases, where the two-state AO expansion method used by GSC becomes more reliable. This implies that the two-state atomic expansion tends to overestimate the cross section at the lower-energy side.

III. CHARGE TRANSFER

In Fig. 2, the present theoretical calculations for the charge transfer to the $H(1s)$ state are compared with the other theoretical calculations[4,5,8] and the three sets of experimental data.[9–11] As we speculated earlier, our cross sections for $H(1s)$ capture are appreciably smaller than those of GSC by a factor of 3 at 1 keV, although this discrepancy is reduced to 22% at 30 keV. However, the shapes of the cross sections are in excellent accord with each other. Theoretical results reported by Hughes and Crothers[7] (not shown) using the low velocity approximation for the two-state-coupled equations seem to agree fairly well with ours in both the magnitude and the shape of the cross section up to 8 keV.

The theoretical study made by Sin Fai Lam,[5] who employed the four-state atomic-orbital expansion method, favors our results qualitatively, despite the fact that his

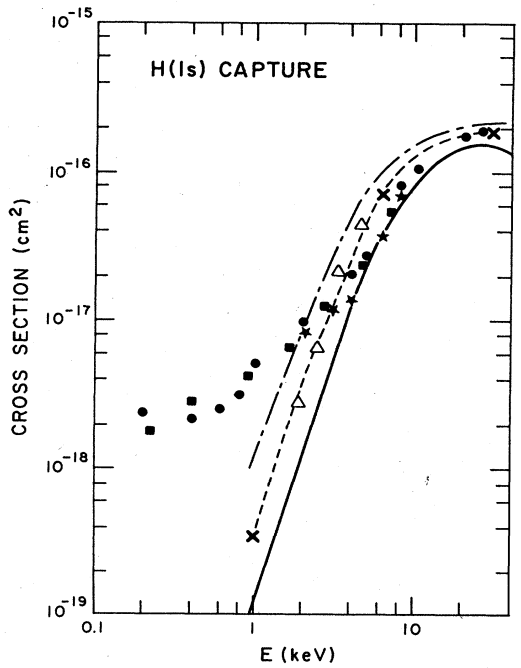

FIG. 2. $H(1s)$-capture cross sections. Theories: solid line, this work; × with broken line, Ref. 4; dash-dot line, Ref. 5; △, Ref. 8. Experiments: ■, Ref. 9; ●, Ref. 10; ★, Ref. 11.

results are a factor of 3 greater than those of GSC. The AO expansion methods used in the calculations (Refs. 4 and 5) do not include He excitation channels in the expansion. Also, the work in Ref. 5 neglects the antisymmetrization of the electronic wave function. These effects should influence the results as an overestimation of the cross section. A conventional two-center AO expansion method employed by GSC and Sin Fai Lam is not regarded as an appropriate method for a close collision in slow ion-atom collisions and it has been recognized recently that inclusion of united atom orbitals in the AO expansion method is essential to treat a close collision in the low-energy region correctly.[14] The four-state MO result by Riera and his colleagues,[8] who ignored ETF's completely, is also plotted in the figure. Because of the defective features such as the origin discrepancy in the PSS theory, they were obliged to choose the center of mass as the origin of the electronic coordinate *a priori*. Their result agrees reasonably well with that of GSC's two-state AO calculation. However, due to their arbitrary choice of the origin, their result may not possess any physical significance. The evidence of good qualitative agreement among the various theoretical approaches previously mentioned in the energy range from 1 keV to 3 keV indicates that the responsibility for the marked disagreement in the H($1s$)-capture cross section lies with the experiments. However, in the medium energy range between 5 and 25 keV, all the theoretical results enjoy qualitative agreement with all the experimental data.

Let us now discuss briefly the cross section for the charge transfer to the H($n=2$) levels [H($n=2$) capture]. The results of the calculated H($n=2$)-capture cross section are displayed along with the experimental data,[15–17] in Fig. 3. For the H($2s$) cross section, the agreement of our values with the experiments[15,16] is satisfactory in the energy region between 2 and 20 keV. Also our results seem to join on to those of Sin Fai Lam[5] above ~ 35 keV, although his results below 25 keV are about a factor of 2 greater than ours. There is, however, some discrepancy between the experiment[15] and the present calculation for electron capture to the H($2p$) level in the lower-energy side where a comparison is possible. Below 8 keV our results fall off appreciably faster than measurements, which is a similar trend found in the discussion of the H($1s$)-capture cross section. The values of Sin Fai Lam are similar qualitatively to the structure of our H($2p$) cross-section results. However, his H($2p$) cross sections are in good agreement with the measurement by de Heer *et al.*,[17] while the present results follow the experimental trend observed by Jaecks *et al.*[15] above ~ 10 keV. The magnitude of the difference between these two theoretical calculations is approximately a factor of 2.

The five-state AO result at 30.16 keV by Winter and Lin[6] is also plotted in Fig. 3. (Their 11-state results, considered the best, agree fairly closely with the five-state results.) Their H($2s$) cross section is a factor of 2 larger than ours, while their H($2p$) cross section is a factor of 2 smaller. Although the two AO results by Sin Fai Lam[5] and Winter and Lin[6] are in good harmony for the H($2s$) cross section at 30.16 keV, the huge discrepancy , seen in the H($2p$) cross section, is puzzling. It would be natural

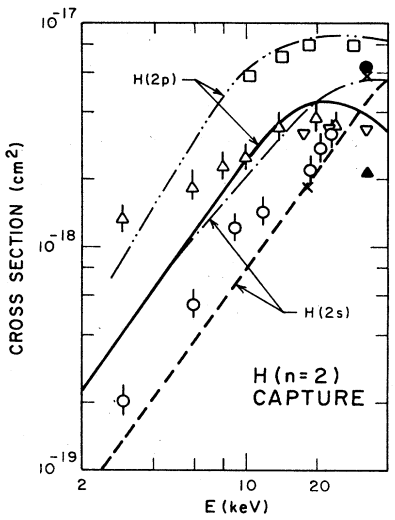

FIG. 3. H($n=2$)-capture cross sections. H($2p$) capture: solid line, this work; dash—double-dot line, Ref. 5; ▲, Ref. 6; △, Ref. 15; ▽, Ref. 16; □, Ref. 17. H($2s$) capture: broken line, this work; dash-dot line, Ref. 5; ●, Ref. 6; ○, Ref. 15; ×, Ref. 16.

to believe that, provided the ETF and the antisymmetrization are correctly taken care of, the AO treatment may offer a more reliable result than the one used here (MO-coupled equations in the first order of **V**) for the calculation of cross sections to Rydberg levels in $v > 1$ a.u.

As we mentioned before, the flux is promoted to higher levels through each of the lower levels sequentially (ladder-climbing mechanism) in the lower-energy regime; neglecting some of the intermediate states in the expansion might introduce a serious error and tend to overestimate the cross section in the lower-energy calculation. Our test calculation, which excluded the He-excitation channels from the expansion (five-states MO calculation), clearly supports the conclusion made above. In fact, the H($2s$) cross section in the test calculation was found to increase by 25% at 10 keV compared to the result obtained by the eight-state MO calculations.

If the energy is greater than ~ 25 keV, the H($2s$)-capture cross sections exceed the H($2p$)-capture cross sections. This is primarily due to the increase of direct capture from the initial state in contrast to the redistribution of the flux from the stepwise promotion in the low-energy case. These results confirm the experimental findings where the shape of the H($2s$) cross-section curve suggests that the H($2s$) cross section may exceed the H($2p$) cross section. As the collision energy increases, the ionization channel becomes the dominant one for the inelastic collisions in the system. Also, the flux loss to the higher Rydberg states is not negligible any more and the present close-coupling method, which does not account for both the ionization and higher-excitation channels, is most likely to overestimate the cross sections. Therefore, the present results for He excitation and H($n=2$) capture in the energy range above 25 keV should be considered to be qualitative. However, the H($1s$)-capture cross section is

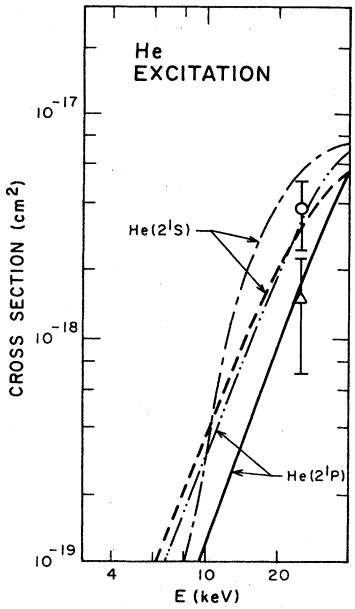

FIG. 4. He-excitation cross sections. He(2^1P) excitation: solid line, this work; dash—double-dot line, Ref. 19; △, Ref. 12. He(2^1S) excitation: broken line, this work; dash-dot line, Ref. 19; ○, Ref. 12.

quite stable in terms of the basis size and considered nearly converged in this energy range studied.

IV. EXCITATION

Consider the He-excitation process. Figure 4 contains the present He(2^1S)- and He(2^1P)-excitation cross sections as well as the experimental cross section.[12] The theoretical results for 2^1S and 2^1P excitation are generally in good accord with the measurement. The result obtained by van den Bos[18] based on the one-center atomic-state (OCAS) expansion calculation show generally close agreement with both the present results and the experiment in the energy range up to 40 keV.

The close agreement of van den Bos's result with the experiment, however, might be fortuitous and needs to be explained carefully. As we pointed out, the stepwise flux-promotion mechanism dominates below 25 keV, where the OCAS method does not account for the mechanism and hence the OCAS method should not be valid. As the energy becomes higher, the OCAS method apparently shares the same difficulty as the molecular-orbital method. And, again, the OCAS method is not reliable.

According to Flannery,[19] he employed the same method that van den Bos used, but he used the improved He-atom wave functions. Therefore, his results are supposedly more accurate. His results are at least 30% larger than those of van den Bos above 15 keV, which is the lowest energy van den Bos studied. Below 15 keV, Flannery's He(2^1P) cross section is a factor of 2 larger than the present cross section over the whole energy range. Flannery's He(2^1S) cross section also exceeds ours by a factor of 2 at energies above ~ 15 keV. However, at ~ 10 keV, his He(2^1S) cross section crosses the present He(2^1S) result and stays lower in magnitude below this collision energy. Also, it should be noted that his He(2^1S) and He(2^1P) cross sections cross over each other around $E \sim 10$ keV, while the present results do not show any crossover of the cross sections below ~ 25 keV. In any case, from the argument made above, the OCAS method itself is questionable, particularly below 25 keV.

V. CONCLUSION

An eight-state close-coupling calculation has been carried out to investigate charge transfer and excitation in $H^+ + He(1s^2)$ collision. The H($1s$)-capture cross-section results are in accord qualitatively with other theoretical results, but in marked disagreement with the experiments below 5 keV. This may be due to experimental error. The H($n=2$)-capture and He-excitation studies show that the stepwise promotion of the flux is an important mechanism below 25 keV. The inclusion of excited He channels in the close-coupling formalism may be of some importance for determining a reliable cross section.

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