"R-matrix" approach to electron transfer in α-H collisions

Thomas G. Winter
Department of Physics, Pennsylvania State University, Wilkes-Barre Campus, Lehman, Pennsylvania 18627 and Department of Physics, Rice University, Houston, Texas 77251*

Neal F. Lane
Department of Physics, Rice University, Houston, Texas 77251

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A mixed, atomic-and-molecular-state approach to heavy-particle collision processes is applied to electron transfer in α-H collisions. Such collisions are difficult to treat at all impact parameters using a pure molecular-state basis without translational factors or a pure atomic-state basis (with plane-wave translational factors) at low-keV energies. It is shown that the use of translational factors in the molecular-state basis may be avoided for internuclear separations $R \leq R_0$ by transforming to an atomic-state basis at $R = R_0$. This "R-matrix" method is shown to be stable over a range of R_0, and a physical criterion is given for determining R_0.

A mixed-basis, or "R-matrix," approach to electron transfer in low-keV-energy ion-atom collisions will be described in the present paper. This method combines the better features of molecular-state and atomic-state approaches, while avoiding their defects. In the following paragraphs, these approaches will be reviewed for α-H collisions of interest here in order to see how the mixed-basis method may be formulated.

Several years ago, Winter and Lane[1] carried out a coupled–molecular-state calculation of cross sections for electron transfer in α-H collisions using what was then a large basis of 20 molecular states $1s\sigma, 2s\sigma, \ldots, 4f\phi$. Several states besides the initial state $2p\sigma$ and resonant charge-transferring states $2s\sigma$, $2p\pi$, and $3d\sigma$ were found to be important: namely, $1s\sigma$, $3p\sigma$, $3d\pi$, $4f\sigma$, and $4f\pi$. This calculation omitted translational factors,[2] and is commonly referred to as a perturbed-stationary state, or PSS, calculation. Subsequently, Hatton, Lane, and Winter[3] and Winter and Hatton[4] included plane-wave translational factors[5] in a basis of ten molecular states $1s\sigma, 2s\sigma, \ldots, 3d\delta$; calculations using different translational factors were carried out by others.[6,7] (The plane-wave factor, molecular-state method is abbreviated MPW.) The MPW results were found to be less sensitive than PSS results to the size of the basis, and probably are more accurate. In tests presented in this paper, 10-MPW results will be used as a standard for comparison. At smaller impact parameters ρ, there is good agreement between PSS and MPW results over a wide range of energies. Unfortunately the agreement is less satisfactory at larger ρ for higher energies: there, the PSS results, even with 20 states, are substantially lower than the MPW results. The inclusion of two more potentially contributing states,[3,4] $5g\sigma$ and $5g\pi$, to form a 22-state basis did not significantly improve agreement; at an energy $E(\alpha) = 8$ keV, the results are still 26% too low at $\rho = 6a_0$, corresponding to the last peak in $\rho P(\rho)$, where $P(\rho)$ is the probability of electron transfer [see Fig. 1(a)].

The defect in the PSS treatment is commonly described as "spurious coupling" among many molecular states at larger internuclear separations R. In the Winter-Lane calculation (for which the proton is taken to be the origin of the coordinate system), this long-range coupling is among states correlating to states of He^+; more important, the coupling between these states—particularly $3d\sigma$—and the initial $2p\sigma$ state on H may also be incorrect, leading to an incorrect transfer of charge from the proton to the α particle. The asymmetric α-H collisions are particularly sensitive to these

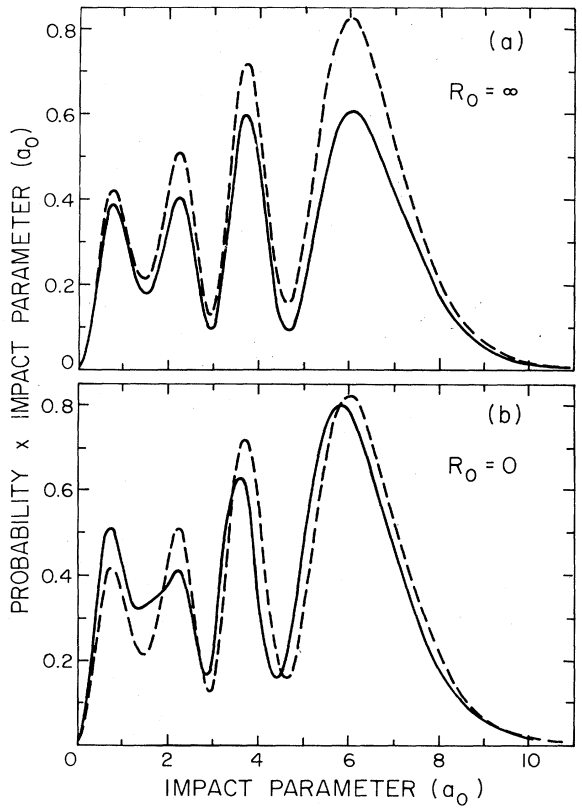

FIG. 1. Probability times impact parameter vs impact parameter for electron transfer in 8-keV α-H collisions. Solid curves: (a) 22-PSS result (i.e., $R_0 = \infty$) (Refs. 3 and 4) and (b) 11-APW (i.e., $R_0 = 0$). Dashed reference curves: 10-MPW result (Refs. 3 and 4). (An energy of 8 keV corresponds to a velocity of 0.283 a.u.)

couplings, since (1) in contrast to symmetric p-H collisions, here several excited states are inherently important, and (2) in contrast to more highly asymmetric collisions, states couple over a wide range of R for which the electronic energy curves are close together.

In an atomic-state treatment with plane-wave translational factors (APW),[8] on the other hand, there are no spurious couplings at larger R. This treatment should thus be more suited to describing electron transfer at larger impact parameters ρ. Consider an 11-APW calculation[9] using the states $1s_{\mathrm{H}}$, $1s_{\mathrm{He}^+}$, $2s_{\mathrm{He}^+}$, ..., $3d_{2\mathrm{He}^+}$; this basis is "analogous" to the 10-MPW basis in the sense that the previously noted 10 molecular states (plus the $4f\sigma$ state) correlate to these 11 atomic states in the separated-atoms limit. It is seen in Fig. 1(b) that at larger ρ, there is good agreement, but at smaller ρ, where a molecular description is more suitable, the APW results are less satisfactory. Thus, the PSS treatment works well at small ρ, say $\rho \leq \rho_0$, while the atomic-state treatment (with plane-wave translational factors) works well at larger ρ, $\rho \geq \rho_0$. This suggests a mixed atomic-and-molecular-basis approach.

A better physical measure of the boundary between the atomic and molecular regions (adopted here) is probably a spherical surface defined by some internuclear separation $R_0 = (\rho^2 + z_0^2)^{1/2}$, where z is the component of $\mathbf{R}$ in the direction of the velocity of the α particle. The approach, then, is to use a PSS basis for $R \leq R_0$ and an APW basis for $R \geq R_0$, leading of course to a more complicated procedure: (1) solve z-dependent coupled-atomic-state equations[9] for $z \leq -|z_0|$, (2) match wave functions at $z = -z_0$, (3) solve molecular-state equations[1] for $-|z_0| \leq z \leq |z_0|$, (4) match wave functions at $z = |z_0|$, and (5) solve atomic-state equations[9] for $z \geq |z_0|$. Since the equations are first order in z, a *single* condition at each matching point suffices to determine the unknown atomic (or molecular) coefficients $a_i(\pm|z_0|)$ in terms of the known molecular (or atomic) ones. A simple procedure is to project the coupled-state expansions of the electronic wave function at $z = \pm|z_0|$ onto the particular basis function corresponding to the unknown coefficient $a_i(\pm|z_0|)$. This contrasts with the quantum-mechanical "R-matrix" method,[10] for which the equations are second order. Since the bases are incomplete, probability is not fully conserved during the matchings: At $E = 8$ keV, the summed probability after two matchings typically lies between 0.91 and 0.99 (and is never less than 0.86) when 22 or 10 molecular states are used in the inner region and 11 atomic states in the outer regions.[11] The electron-transfer probabilities presented below have been normalized by dividing by this summed probability.

The utility of this mixed-basis method of course depends on the lack of sensitivity of the results to the matching radius R_0. Consider results at 8 keV using a 22-PSS basis for $R \leq R_0$ and an 11-APW basis for $R \geq R_0$. The choice $R_0 = 10\ a_0$ yields results (not shown) almost identical with the fully PSS 22-state results[12] (i.e., $R_0 = \infty$; in Fig. 1). Therefore, the radius $R_0 = 10a_0$ is unsatisfactory, presumably too large. Consider now graphs of $\rho P(\rho)$ using matching radii R_0 from 3 to 7. Some of these results are shown in Fig. 2. At the second, third, and fourth peaks, all values of R_0 in the range 3–7 yield closer agreement with MPW results than does the value $R_0 = \infty$. (The agreement at the first peak is good—within 8% over the large range $R_0 = 4$–∞.) Further, with the exception of the second peak for $R_0 = 5$, values of R_0 in the smaller range 5–7 yield

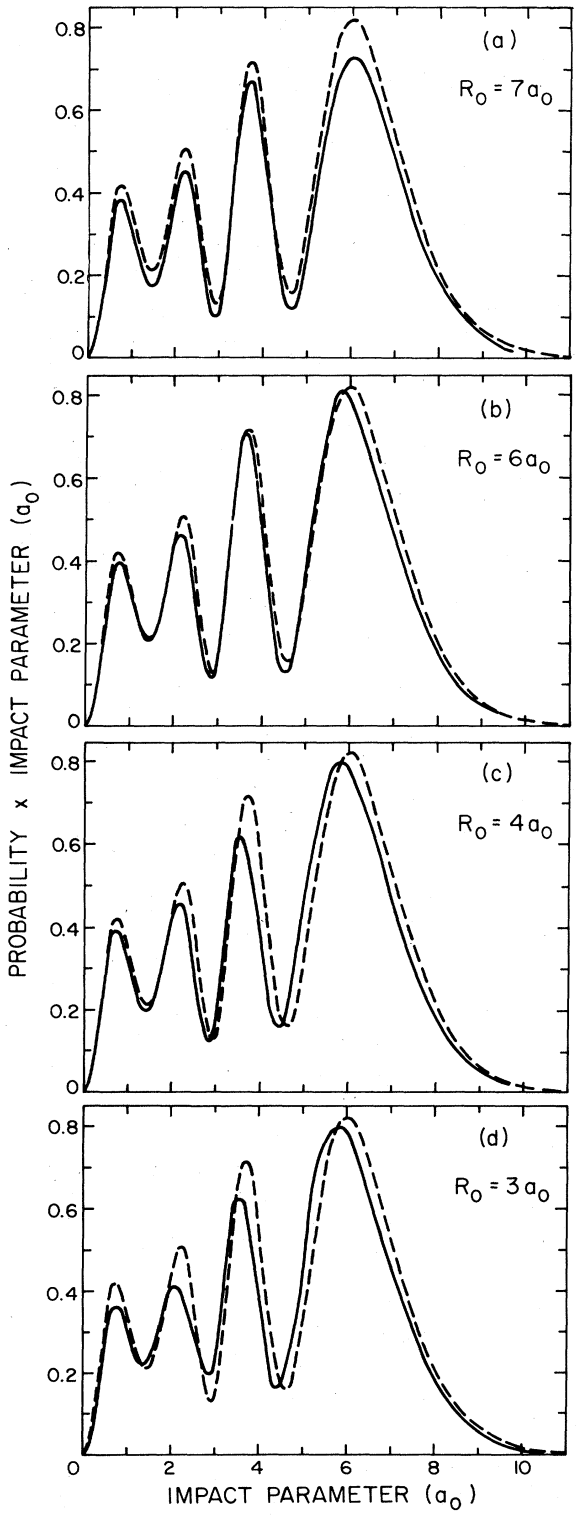

FIG. 2. As in Fig. 1, except solid curves are mixed-basis results for matching radii $R_0 = 3$–7.

agreement with MPW results at least a factor of 2 better than does the value $R_0 = \infty$. With $R_0 = 3$ or 4, larger differences from MPW results at the second and third peaks probably reflect the lesser quality of the atomic-state basis there, inasmuch as the range of z is small (or zero) in the

inner region for these cases. The point we want to emphasize is that for R_0 between 4 and 7, these mixed-basis results are as good as PSS results at small ρ and APW results at large ρ, and nearly as good as 10-MPW results at all ρ.

A rough overall measure of the quality of the mixed-basis approach is the comparison in Table I of total cross sections

$$Q = 2\pi \int_0^\infty d\rho\, \rho P(\rho)$$

since, for $R_0 > 0$, differences in the integrands $\rho P(\rho)$ with the mixed basis and the MPW basis are always of the same sign (ignoring slight phase differences).[13] Also shown in Table I are mixed-basis values of cross sections corresponding to a 10-PSS basis in the inner region. The results are not as good as when using a 22-PSS basis, and the matching radii must be smaller since some longer range molecular functions, important here, have been omitted.

There is a simple explanation for why the intermediate values $R_0 = 5$–6 yield the best results (3–7 if less accuracy is required). It is seen in Fig. 3 for $\rho = 6.11$ (the location of the fourth peak) that the electron cloud[14] is just beginning to break in two at $R_0 \simeq 6$–8; a similar situation holds for the third peak (not shown). (The breakup presumably is beginning when the contours start to close on themselves.) It is critical that R_0 be no larger than this radius, since for larger R, the electron cloud is largely atomic in character. In order for the proper amount of this cloud to attach itself to the charge-transferring nucleus, the appropriate atomic translational factor must be included to allow the basis functions to translate with that nucleus. An insufficient transfer, or too small an electron cloud on α, will occur if a fully PSS basis, and origin on the proton, is used (not shown), and presumably too much transfer occurs if the origin is placed on the α particle. This consideration is particularly important for α-H collisions, in which transfer occurs gradually, over some distance. The proper choice of translational factors of course eliminates the spurious couplings previously referred to.

Recently, Kimura and Lin[15] have carried out an "R-matrix" calculation for electron transfer in the "inverse" p-He^+ collision. This collision is quite different since the initial and primary final wave functions are $1s_{He^+}$ and $1s_H$, respectively, which only overlap over a very short range.[16] Therefore, (1) fewer molecular basis functions are required and (2) there is less difference between molecular-state results using different (or no) translational factors. This implies even greater stability with respect to variations in

TABLE I. Ratio $Q_{N,R_0}/Q_{10}$ of cross sections for electron transfer in 8-keV α-H collisions, where $Q_{10} = 6.35\times10^{-16}$ cm^2 is the 10-MPW value (Ref. 3) and Q_{N,R_0} is the mixed-basis value using $N = 22$ or 10 PSS (and origin on the proton) for $R \leq R_0$ and 11 atomic states for $R \geq R_0$. If $R_0 = \infty$, then the basis is fully molecular.

R_0	$N=22$	$N=10$
∞	0.781	0.603
10	0.776	0.582
7	0.878	0.711
6	0.932	0.820
5	0.956	0.905
4	0.938	0.913
3	0.945	0.933

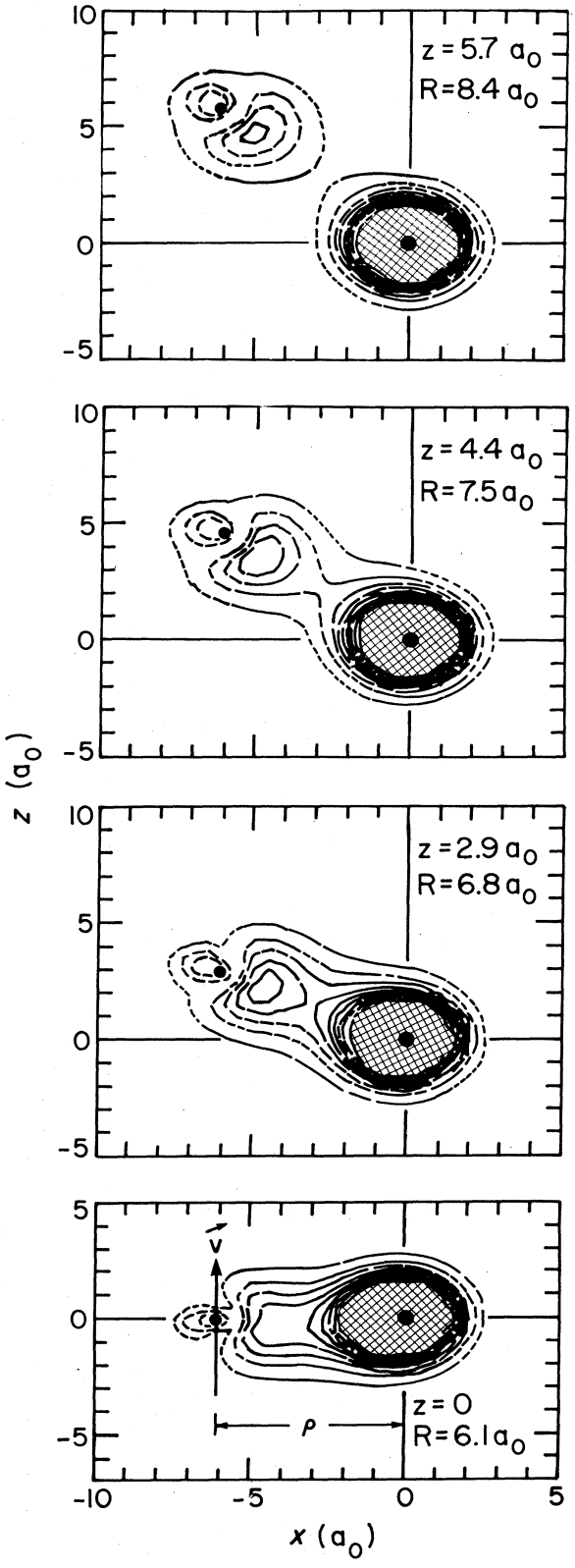

FIG. 3. Electronic probability density in the collision plane $y = 0$ for 8-keV α-H collisions using a 10-MPW basis. The coordinates (x,z) of the α particle and proton are $(-\rho,z)$ and $(0,0)$, respectively. The high density centered on the proton has been truncated.

R_0; indeed they have found results stable out to $R_0 \simeq 10$–12. Their study, combined with the present one, on a perhaps more difficult collision process, shows that the mixed-basis approach holds promise for eliminating the need for translational factors in molecular bases.[17]

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*Permanent address.

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[9]Using the computer program of Winter (Ref. 8).

[10]E. P. Wigner and L. Eisenbud, Phys. Rev. **72**, 29 (1947).

[11]This summed probability oscillates as a function of ρ, with smaller variations, and a value closer to unity, at larger values of ρ.

[12]Values of $\rho P(\rho)$ at each of the four peaks using $R_0 = 10$ and ∞ agree to at least 3% (and are in phase). Thus, it does not agree very well with the MPW result except at the first (smallest ρ) peak.

[13]For $R_0 = 0$ (the fully atomic case), the ratio of cross sections as defined in Table I is fortuitously nearly unity (0.993) since at small ρ differences in the integrands are not of constant sign [see Fig. 1(b)].

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[17]There exist two earlier mixed-basis calculations using small bases of 2-3 states: A. S. Dickinson and R. McCarroll, J. Phys. B **16**, 459 (1983) and A. Salin, *ibid.* **16**, L661 (1983). In a model calculation, Salin has shown analytically that these results are strongly sensitive to the choice of R_0. However, in view of the present results and those of Kimura and Lin, this sensitivity may reflect the smallness of the basis (2 states) used by Salin. Provided the basis is sufficiently large, and provided R_0 is chosen to be in a suitable range, cross sections may be determined accurately, at least for capture into all states.