

Unified treatment of slow atom-atom and ion-atom collisions

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A unified treatment of slow ion-atom and atom-atom collisions for many-electron systems is proposed. The time-dependent electronic wave function is expanded in terms of traveling atomic orbitals of the two collision centers at large internuclear separations and is matched to the solution in the inner region where it is expanded in terms of molecular orbitals without translational factors. It is shown that this method avoids the difficulties associated with the conventional perturbed-stationary-state approximation. Application to charge transfer in the $H^+ + He^+$ collision is illustrated.

Since the early work of Massey and Smith,¹ it has been well recognized that electronic processes in slow ion-atom and atom-atom collisions can be understood qualitatively in terms of the perturbed-stationary-state (PSS) approximation. In this model, one notes that in slow collisions the electrons move much faster than the nuclei so that the time-dependent electronic wave function can be expanded using molecular orbitals of the collision complex. This simple model has been widely used in the interpretation of experimental data and in many model calculations.² However, in *ab initio* calculations, the PSS model cannot be implemented directly. The fundamental difficulty is that each molecular orbital at asymptotic separation does not satisfy scattering boundary conditions and that the PSS formalism is not Galilean invariant.

This difficulty was first discussed by Bates *et al.*³ They pointed out that some velocity-dependent phase factors should be incorporated into the molecular orbitals in the PSS model. These factors, called electron translation factors (ETF's), stress the fact that the electrons are moving with one or the other collision center. In recent years, several different forms of ETF's have been suggested⁴ and *ab initio* calculations based on such formulations are gradually emerging. Except for very few instances, however, all of these calculations are limited to one-electron and quasi-one-electron systems.

In this paper we propose a new approach for slow atomic collisions for many-electron systems. This approach eliminates all the difficulties associated with the PSS model and the ambiguities of choosing ETF's in the many-electron collision systems. Our basic idea is similar to the *R*-matrix method⁵ used in the time-independent formulation of scattering in quantum mechanics. Within the semiclassical impact parameter approximation, we recognize that at large internuclear separations, $R \geq R_0$ (R_0 is a chosen parameter), where the charge clouds do not significantly overlap, the time-dependent electronic wave function is naturally expanded in terms of traveling atomic orbitals (AO) of the two moving centers. In the interaction region $R < R_0$, the electrons from the two col-

lision centers strongly overlap and this inner region should be solved variationally. For slow ion-atom and atom-atom collisions, however, the inner region can be conveniently expanded in terms of molecular orbitals (MO). In this region, the electrons are not clearly moving with either center. Thus, in the center-of-mass system, no ETF's need to be applied. The solutions in the two regions are matched at R_0 . Therefore, in this AO-MO matching method, the time-dependent Schrödinger equation is expanded in terms of two-center traveling atomic orbitals in the outer region and the resulting first-order coupled equations are integrated from $t = -\infty$ to t_1 ($t_1 < 0$), where $R(t_1) = R_0$. At R_0 , this solution is expanded in terms of static molecular orbitals (if the origin is fixed at the center of mass). The expansion coefficients serve as initial conditions for the integration of the coupled equations within the MO framework from t_1 to t_2 ($t_2 > 0$), where $R(t_2) = R_0$. At t_2 , the solution is matched to expansions using two-center traveling atomic orbitals to find expansion coefficients which serve as initial conditions for the integration of the coupled equations within the AO framework from t_2 to ∞ to extract scattering amplitudes.

This AO-MO matching procedure clearly depends on how well the solutions at R_0 can be matched by the two basis sets. Obviously, if R_0 is chosen to be too small, then a large AO basis set is needed. On the other hand, a large R_0 would require a large MO basis set. An optimum choice of R_0 is where the dominant molecular orbitals are adequately represented by a linear combination of atomic orbitals (LCAO).

We remark here that in this AO-MO matching procedure, the inner region is completely analogous to the PSS method. Thus qualitative interpretations about any collision system can still be obtained based upon the behavior of the relevant MO's. On the other hand, all the formal fundamental difficulties associated with the PSS model are eliminated.

(1) Since the MO expansion is only limited to the $R \leq R_0$ region, the problem associated with the incorrect

asymptotic boundary conditions at $t \rightarrow \pm \infty$ no longer arises. The traveling two-center atomic orbitals in the outer region satisfy boundary conditions correctly.

(2) Unlike the PSS method, this procedure retains Galilean invariance. As the origin of the coordinate system is changed, suitable plane-wave translational factors should be incorporated. For example, if the origin is shifted to the target center, a common plane-wave ETF factor, $\exp(iv_{c.m.} \cdot \mathbf{r})$, should be attached with all the molecular orbitals. This will result in different initial conditions at t_1 and t_2 to compensate for the change of coupling matrix elements due to the change of origin.

The major advantage of this AO-MO matching method is its ready application to many-electron systems. By disregarding ETF's in the inside region, the conceptual difficulties of assigning *a priori* ETF's for many-electron molecular wave functions are avoided. In this regard, the various codes developed by quantum chemists for structure calculations can be applied directly to obtain potential curves and coupling matrix elements for collision calculations. In the outer region, exchange symmetry for electrons from different collision centers can be neglected and plane-wave ETF's can be assigned to each electron on each center uniquely.

We have employed this matching procedure to calculate total charge transfer probabilities in $H^+ + He^+(1s)$ collisions at collision velocities from $v=0.2$ to 0.55. This system has been investigated by various authors using different models.⁶⁻⁸ In particular, Kimura and Thorson⁶ studied the same system using a MO-based close-coupling calculation where semianalytical ETF's were attached to each MO throughout the whole range of R . In Fig. 1, we compared the calculated impact-parameter weighted total capture probabilities at $v=0.28$, 0.45, and 0.55. From Fig. 1(a) we note that the result from the present AO-MO matching (shown as solid line) agrees almost exactly with the result from the MO calculation (shown as solid circles) at $v=0.28$. The agreement at the two higher velocities are also quite good, both in shape and in magnitude, with the discrepancy becoming more noticeable at $v=0.55$. In our present calculation, $R_0=3$ a.u., the origin was taken at the center of mass, and the molecular orbitals used are: $1s\sigma[He^+(1s) + H^+]$, $2p\sigma[He^{++} + H(1s)]$, $3d\sigma$ and $2s\sigma[He^+(2s + 2p_0) + H^+]$, and $2p\pi[He^+(2p_{\pm}) + H^+]$; the atomic states used are: $1s$ of

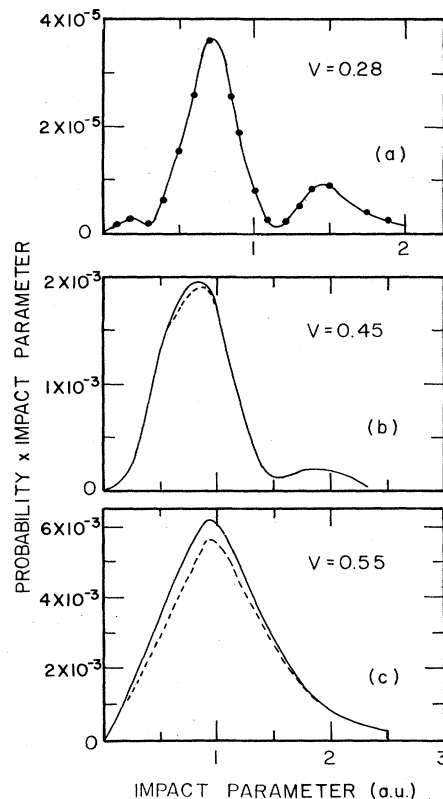


FIG. 1. Impact-parameter weighted charge-transfer probabilities vs impact parameter for $H^+ + He^+(1s) \rightarrow H(1s) + He^{2+}$ collisions at (a) $v=0.28$, (b) $v=0.45$, and (c) $v=0.55$ a.u. Shown as the solid line is the result from the present AO-MO matching procedure. The results from the MO-based calculation of Kimura and Thorson (Ref. 6) are shown as the solid circles in (a) and as the dashed lines in (b) and (c).

H, and $1s$, $2s$, $2p_0$, and $2p_{\pm}$ of He^+ . The molecular states used in this calculation are exactly identical to the ones used in the MO calculation of Ref. 6, except that we do not have ETF's and MO's are used only inside R_0 , while in Ref. 6 ETF's are attached to each MO throughout the whole range of R .

To check the sensitivity of the calculated capture probability on the parameters used in the matching procedure,

TABLE I. Dependence of capture probability $P(\rho)$ on matching parameters. The study is made for $\rho=0.7$ for $v=0.28$ and $\rho=0.8$ for $v=0.45$. For the types of MO's included, see the text. Numbers in parentheses signify powers of ten; e.g., $0.509(-4) = 0.509 \times 10^{-4}$. c.q. denotes center of charge and c.m. denotes center of mass.

No. of MO basis	R_0 (a.u.)	Origin	$P(\rho)$	
			$v=0.28$ $\rho=0.7$	$v=0.45$ $\rho=0.8$
5	3	c.m.	0.509(-4)	0.234(-2)
	4		0.519(-4)	0.240(-2)
5	3	c.q.	0.499(-4)	0.225(-2)
		c.m.	0.509(-4)	0.234(-2)
		H	0.483(-4)	0.220(-2)
		He	0.520(-4)	0.236(-2)

we have studied the effects of (a) the change of matching parameter R_0 , and (b) the change of origin of the coordinate system. In Table I, we listed the results of such comparisons at $v=0.28$ and 0.45 at the impact parameter where the impact-parameter weighted-capture probability is maximum. (The quoted numbers probably have more digits than the actual numerical accuracy would support.) In each case, the variation of capture probabilities is less than a few percent.

We also note that the total capture cross sections, obtained from Fig. 1 by integrating over impact parameters, are nearly identical for the two calculations. These total cross sections are in good accord with experimental data,⁹ as shown in Ref. 6. The small discrepancy at $v=0.55$ and at higher velocities has to be further examined by enlarging the basis set in each model calculation.

To show that the present method also gives reasonable results for small channels, we have also calculated the total excitation cross sections to $2s$, $2p_0$, and $2p_{\pm 1}$ states of He^+ at $v=0.28$ and 0.45 . These results are compared with the five-state MO expansion calculations of Kimura and Thorson and of Winter *et al.* in Table II, where different ETF's are used in the latter two calculations. The discrepancies among the three approaches are acceptable in view of the small number of basis functions used in each calculation. At present there is no experimental data for comparison.

In summary, we have proposed a new AO-MO match-

TABLE II. Excitation cross sections to $n=2$ levels for $\text{H}^+ + \text{He}^+(1s)$ collisions (units 10^{-16} cm^2). Kimura and Thorson (KT5) (Ref. 6); Winter, Hatton, and Lane (WHL5) (Ref. 8); AOMO, present result.

		$\text{He}^+(2s)$	$\text{He}^+(2p_0)$	$\text{He}^+(2p_{\pm 1})$
$v=0.28$	KT5	3.68(-6)	3.21(-6)	7.10(-6)
	WHL5	6.51(-6)	5.62(-6)	7.95(-6)
	AOMO	4.55(-6)	3.80(-6)	6.31(-6)
$v=0.45$	KT5	2.56(-4)	2.38(-4)	3.56(-4)
	WHL5	3.08(-4)	4.06(-4)	4.20(-4)
	AOMO	3.94(-4)	3.14(-4)	4.00(-4)

ing method for calculating inelastic electronic processes in slow ion-atom and atom-atom collisions. This method eliminates all the difficulties associated with the perturbed stationary state approximation. Initial application to charge transfer in $\text{H}^+ + \text{He}^+$ collisions indicates that the result is very stable against the change of matching parameter R_0 and the shift of origin in the coordinate system. This method can be applied directly to collisions involving many-electron systems.

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