CONF-830390--1

ATOMIC-ORBITAL EXPANSION MODEL FOR DESCRIBING ION-ATOM COLLISIONS AT INTERMEDIATE AND LOW ENERGIES#

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CONF-830390--1

DE83 017553

Introduction:

In the description of inelastic processes in ion-atom collisions at moderate energies, the semiclassical close-coupling method is well established as the standard method. Ever since the pioneering work[1,2] on $H^+ + H$ in the early 60's, the standard procedure is to expand the electronic wavefunction in terms of molecular orbitals (MO) or atomic orbitals (AO) for describing collisions at, respectively, low or intermediate velocities. It has been recognized since early days that traveling orbitals are needed in the expansions in order to represent the asymptotic states in the collisions correctly. While the adoption of such traveling orbitals presents no conceptual difficulties for expansions using atomic orbitals, the situation for molecular orbitals is less clear. In recent years, various forms of traveling MO's have been proposed, but conflicting results for several well-studied systems[3] have been reported.

The Two-Centered AO Expansion:

A conventional AO expansion is frequently regarded as appropriate for collisions at intermediate velocities but not for slow collisions since the relaxation of the electronic orbitals is not taken into account. However, it is known that MO's at large internuclear separations can be represented by two-center AO expansions (linear combination-of-atomic-orbitals (LCAO) methods with AO's of the separated atoms (SA), thus it is obvious that the conventional AO expansions are also adequate for describing slow collisions at large impact parameters. For near-symmetric collisions, charge transfer occurs at relatively large impact parameters over a large energy range. Thus the total electron capture cross sections as well as capture probabilities at large impact parameters can be accurately predicted by the conventional AO expansion. For example, recent experimental electron transfer cross sections of K-shell electrons to the K-shell of bare projectiles determined from inner-shell processes in ion-atom collisions have been accurately predicted by the simple two-state atomic expansion (TSAE) model.[4] In this model, the AO expansion is truncated to include the 1s orbitals of the projectile and of the target only. Comparison of TSAE predictions with experimental results has been summarized recently by Lin and Richard.[5]

The AO+ Model:

The conventional AO expansion is not useful for describing slow collisions at small impact parameters. In particular, it is well known that the MO's at small internuclear separations cannot be represented by the LCAO

method. There, however, MO's can be expanded in a set of united-atom (UA) orbitals. We have, therefore, recently proposed a modified atomic expansion (AO+) model[6] in which AO's of the separated atoms and of the united atom are incorporated in a close-coupling expansion. Starting from such an expansion, the low-energy "molecular features" of the collision systems are well represented, as is indicated by the accurate molecular correlation diagrams calculated from AO+ expansion sets. In dynamical calculations within the AO+ expansion model, however, the formal difficulties of using molecular translational factors are avoided. Thus calculations within the AO+ model can be performed for a broad range of energies covering the intermediate and low-velocity region.

The AO+ model has now been applied to a few well investigated collision systems.[7] Some of the results will be presented.

Including Ionization Channels:

For near-symmetric collisions at intermediate velocities, ionization cross sections become comparable or greater than excitation and charge transfer to low-lying bound states. In close-coupling calculations, such ionization channels are often not considered. In one of our recent works we have shown that the failure of including ionization channels has resulted in the overestimate of cross sections to low-lying states. To incorporate ionization channels into our AO+ model, we represent the continuum wavefunctions by square-integrable functions. These pseudostates are obtained by diagonalizing the SA Hamiltonian within a set of Slater orbitals. We emphasize that the precise nature of these pseudostates is not important except that there should be a few ($3 \sim 4$) pseudostates with energies within $1 \sim 2$ a.u. above the threshold. We have recently applied this model to $H^+ + H$ collisions within the 1 - 75 keV region.[8] Our results indicated that experimental excitation and charge transfer to n = 2 and n = 3 states and total ionization cross sections over the indicated energy region are now well predicted by this model.

References:

#Work supported by Department of Energy, Division of Chemical Sciences.

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