§10. Study of Low-Energy Ion-Atom Collisions by the AO-MO Matching Method

Shimizu, F., Toshima, N. (Univ. Tsukuba)
Tawara, H.

The close-coupling method has achieved a status as the most reliable theoretical technique for the study of ion-atom collisions. The scattering wave function is expanded as a linear combination of basis functions and the resulting coupled equations are solved numerically. Except for an extremely low collision-energy region below some tens of eV, the semiclassical description by the impact parameter method is valid. Two types of basis functions have been used in actual calculations complementarily; atomic-orbital (AO) expansion for the case that the velocity of the incident projectile is larger than that of the bound electron(s) and molecular-orbital (MO) expansion in the opposite case. The latter approach is based on an apparently sound physical picture that the nuclei and the electron form a quasi-diatomic-molecule during the collision for slow collision, but it has an intrinsic difficulty associated with the physical boundary condition in the asymptotic region where the electron can not be shared by the two nuclei. While the AO expansion is free from this difficulty and still valid even for the low-energy collisions, we need a rather large number of basis functions to get well-converged cross sections there.

The AO-MO matching method[1,2] is a hybrid procedure in which the AO expansion is used in the outer region and the MO expansion in the inner region. The two solutions are matched to each other at a certain boundary by a frame transformation. This method removes the above-mentioned difficulty of the MO expansion and besides improves the slow convergence of the AO expansion in the inner region.

In the present AO-MO matching calculations we develop new numerical techniques in both the AO and the MO expansions. Firstly, in the AO expansion, we do not attach the electron translation factors explicitly in the basis functions but take them into account by diagonalizing the effective Hamiltonian that represents atomic states moving with a finite velocity. This novel technique drastically simplifies the evaluation of the the coupling matrix elements and makes the extension to multielectron systems easier. Secondly, the diabatic-sector-method is applied to the solution of the coupled equations in the MO expansion. We divide the inner region into a number of small sectors. In the nth sector, $(R_{n-1} + R_n)/2 \leq R \leq (R_n + R_{n+1})/2$, the scattering wave function is expanded in terms of locally diabatic basis functions constructed from molecular orbitals at a fixed internuclear distance R_n. The solution of the coupled equations in each sector is propagated successively to the next sector by projecting it to the next basis functions. This procedure removes the difficulty arising from the nearly singular structure of the radial couplings near avoided-crossing points.

Numerical calculations are now under execution. Further details and numerical results will be shown in a forthcoming paper.

References

1) M. Kimura and C.D. Lin, Phys. Rev. **A31**, 590 (1985); ***ibid.*** **32**, 1357 (1985).
2) T.G. Winter and N.F. Lane, Phys. Rev. **A31**, 2698 (1985).