quantum symmetry preserving semiclassical method

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(eceived uly accepted ugust)

ymmetry constraints are built into a semiclassical propagation scheme t is then applied to treat + e collisions at where quantum selection rules restrict the final rotational states of symmetric e molecules to the even manifold The cross sections for state to state transitions are calculated for symmetric and nonsymmetric isotopic compositions of e II bound and long lived quasibound (trapped behind the centrifugal barrier) states of e are considered This semiclassical method captures symmetry effects and shows satisfactory agreement with the quantum results © 2002 American Institute of Physics. []

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ost semiclassical methods for molecular collisions give results that violate symmetry selection rules n this ar ticle we demonstrate a way to maintain the quantum property of symmetry using semiclassical methods or transparency we use the simplest version of the semiclassical method pro posed by eller and known as the frozen aussian wave packets method evertheless our approach is general and it is straightforward to use it with more sophisticated and accurate semiclassical methods such as the erman– luk () propagator is

which the initial state of e is the ground rovibrational state v = j = at a total energy of n Table we show state to state cross sections for transitions to all bound and quasibound states for three different isotopic combinations of the e molecule—two symmetric combinations e e and e e and one nonsymmetric combination e e s discussed in ppendix symmetric mol ecules exist only in even rotational states (a total of states in T



 $\dot{\gamma}_n = {}^{\mathbf{p}_n}$

There the amplitude of the wave function [q()] is very small or each *j* value this part of space is identified and is not covered by aussians

econd we assign the initial momenta \mathbf{p}_n to the wave packets to obey qs ()-() n ppendix it is shown that (for j > j if the position \mathbf{r}_n is chosen anywhere between the turning points then four different \mathbf{p}_n vectors satisfy qs ()-() and so we start four wave packets from each such point f the initial position \mathbf{r}_n is a turning point then only two different \mathbf{p}_n vectors satisfy qs ()–() and we start only two wave packets from the turning points f_{j} = then these are reduced to two wave packets starting from any point between the turning points and one wave packet start ing from any turning point This simplest situation is shown ere we decided to place four initial wave packets in ig in each radial direction Two of them start at the turning points with no initial momenta. The other two start in the middle between the turning points with equally valued but oppositely directed radial momenta When j > additional tangential components of momenta appear (see ppendix) and the picture becomes more complex

fter the upper hemisphere is covered by aussians we reflect their positions and momenta through the center of the sphere onto the lower hemisphere This finalizes the sam pling procedure

ur sampling procedure produces trajectories "on the energy shell" as opposed to onte arlo sampling from a Wigner space distribution We need to use "on the energy shell" trajectories because we also want to describe the qua sibound long lived states of the e molecule (see ppendix

) with the same procedure that we use for bound states lassical trajectories may be prepared at the energy of a

In a lived quasibound state with appropriate initial conditions so that they remain trapped forever behind the centrifucal barrier. These trajectories permit us to reasonably detribe quasibound states in the contrary. Wigner space ampling would produce some trajectories at energies above the centrifugal barrier and allow the e molecule to disso date even without colliding with the atom. These events would create a problem in the present study.

ow do we capture the effect of symmetry

et us consider two wave packets placed symmetrically at the initial moment of time We will call them the "+" and the " just by a sign $\nabla_{\mathbf{r}} V \mathbf{r}^+ = -\nabla_{\mathbf{r}} V \mathbf{r}^-$ ut for the case of a *nonsymmetric* e molecule where the two e atoms have different masses the two arrangements of the <u>e</u> "collision complex" are different [ig (b)] because of the slight shift in the center of mass of the e s a result the potentials and the gradients will be different for the "+" and "-" wave packets

et us consider first the *symmetric* case [ig (a)] ach aussian wave packet is propagated independently during the collision with the atom evertheless each pair of wave packets placed symmetrically at the initial moment of time will remain symmetric in its motion as the atom evolves along its trajectory $\mathbf{R} \ t$ This is clearly seen from the equations of motion [qs ()–()] for the two wave packets or the "+" wave packet we have

$$\mathbf{r}^{+}(t) = \mathbf{r} + \int^{t} \frac{\mathbf{p}^{+}(t)}{\mu} dt \qquad ()$$
$$\mathbf{p}^{+}(t) = \mathbf{p} - \int^{t} \nabla_{\mathbf{r}} V(\mathbf{r}^{+} t) d$$

 $\langle b$

$$S_{ba}^{()} = S_{ba}^{()} - S_{bb}^{()} \frac{\langle b | \phi_a \rangle}{\langle a | \phi_a \rangle} = \frac{\langle b | \psi_a \rangle}{\langle a | \phi_a \rangle} - S_{bb}^{()} \frac{\langle b | \phi_a \rangle}{\langle a | \phi_a \rangle} \quad b \neq a$$
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rossmann hys ev 57 ( )
rossmann and Xavier r hys ett 243 ( )
ay hem hys 100 ( )
ay hem hys 100 ( )
ay hem hys 101 ( )
Zor and ay hys ev ett 76 ( )
adhusoodanan and ay hem hys 109 ( )
Y Iran and ay hem hys 114 ( )
V halashilin and hild hem hys 113
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