

Supporting information for

**An effective approximation of Coriolis coupling in reactive
scattering: Application to the time-dependent wave packet
calculations**

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Theoretical method

In this work, we present the TDWP method in more detail using the atom-diatom reactions (A + BC) as an example. For the TDWP method¹⁻³, the Hamiltonian in reactant Jacobi coordinates for a conserved total angular momentum J can be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} + \frac{\hat{L}^2}{2\mu_R R^2} + \hat{h}(r) + \hat{V}(R, r, \theta) \quad (1)$$

with

$$\hat{h}(r) = -\frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} + \frac{\hat{j}^2}{2\mu_r r^2} + V(r) \quad (2)$$

where L and j are the orbital diatomic rotational angular momentum quantum numbers, respectively. μ_R and μ_r are the reduced masses for the two radial Jacobi coordinates (R , r), respectively. $\hat{V}(R, r, \theta)$ is the atom-diatom interaction potential, and $V(r)$ is the diatom potential energy curve. The total time-dependent wavefunction of the system can be expanded in terms of the translational-vibrational-rotational basis as⁴⁻⁶

$$\Psi^{JM_p}(\mathbf{R}, \mathbf{r}, t) = \sum_{nvjK} F_{nvjK}^{JM_p} u_n(R) \phi_v(r) y_{jK}^{JM_p} \quad (3)$$

where p is the parity of the system. M and K are the components of the total angular momentum on the space-fixed (SF) z axis and the BF z axis. The translation basis functions $u_n(R)$ are chosen as the *sine* function with an equidistant discrete variable representation (DVR)⁷ grid. The vibrational basis set $\phi_v(r)$ is the eigenfunction of the BC molecular Hamiltonian. For the angular part, the parity-adapted BF basis can be written as¹

$$y_{jK}^{JM_p} = D_{MK}^{Jp}(\Omega) y_{jK}(\cos \theta) \quad (4)$$

where $D_{MK}^{Jp}(\Omega)$ is the parity-adapted normalized Wigner rotation matrix⁸ that only depends on Euler angles Ω , and $y_{jK}(\cos \theta)$ are spherical harmonics. In this representation, rotational angular momentum \hat{j} and orbital angular momentum are coupled to \hat{J} . The quantum number K ranges from 0 to J for even total parity and from 1 to J for odd total parity.

In the TDWP method, the time-dependent Schrödinger equation can be solved by the second-order split-operator scheme^{9, 10}

$$\psi(t + \Delta) = \exp^{-i\hat{V}\Delta/2} \exp^{-i\hat{V}_{rot}\Delta/2} \exp^{-i\hat{T}\Delta/2} \exp^{-i\hat{V}_{rot}\Delta/2} \exp^{-i\hat{V}\Delta/2} \psi(t) \quad (5)$$

$$\text{with } \hat{V}_{rot} = \frac{(\hat{J} - \hat{j})^2}{2\mu_R R^2} + \frac{\hat{j}^2}{2\mu_r r^2} \quad \text{and} \quad \hat{T} = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} + \hat{V}(r)$$

where t is the propagation time and Δ the time interval. For the dynamic calculations of a non-adiabatic reaction involving two coupled electronic states, the potential energy operator \hat{V} can be written as a 2×2 off-diagonal matrix as follows:

$$\hat{V} = \begin{bmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{bmatrix} \quad (6)$$

Because the potential energy operator is not diagonal in the diabatic representation, it is necessary to convert it to the adiabatic representation:

$$\begin{aligned} \exp(-i\hat{V}\Delta_t / 2) &= \exp(-i \begin{bmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{bmatrix} \Delta_t / 2) \\ &= \mathbf{T}^{-1} \begin{bmatrix} \exp(-iE_1\Delta_t / 2) & 0 \\ 0 & \exp(-iE_2\Delta_t / 2) \end{bmatrix} \mathbf{T} \end{aligned} \quad (7)$$

where E_i ($i = 1, 2$) and \mathbf{T} are the eigenvalues and eigenvectors of the diabatic potential energy matrix respectively, which can be obtained by diagonalizing eq (6).

Consequently, the scattered wave function can be obtained by evaluating the effect of the Hamiltonian on the propagating wave packet, that is, matrix-vector multiplication. In addition, the initial wave packet needs to be determined before its propagation. The wave packet with a definite initial state (v_0, j_0, l_0) can be constructed as^{1, 11}

$$\Psi_{v_0 j_0 l_0}^{JMp}(t = 0) = G(R) \phi_{v_0 j_0}(r) Y_{j_0 l_0}^{JM}(\cos \theta) \quad (8)$$

where $\phi_{v_0 j_0}(r)$ is the initial rovibrational eigenfunction of BC diatom, $y_{j_0 l_0}^{JM}(\cos \theta)$ is the total angular momentum eigenfunction in the SF representation, and $G(R)$ is a Gaussian function with the position R_c and width δ

$$G(R) = \left(\frac{2}{\pi\delta^2} \right)^{1/4} \exp \left[-\frac{(R - R_c)^2}{\delta^2} - i\sqrt{2\mu_R E_c} R \right] \quad (9)$$

The propagation of the wave packet is conveniently performed in the BF frame since the BF z-axis is chosen to be along the vector R . The initial wave pack with selected initial quantum state (v_0, j_0, K_0) in the BF representation can be obtained by¹

$$y_{j_0 K_0}^{JMp} = \sum_{l_0} C_{l_0 K_0}^{J j_0 p} Y_{j_0 l_0}^{JM} \quad (10)$$

where $C_{l_0 K_0}^{J j_0 p}$ is defined as the parity-adapted orthogonal transformation matrix.

The main task of the TDWP calculations is the action of the Hamiltonian matrix on the wave vector. Evaluating the action of individual operators in eq (5) in appropriate representations is the most efficient means. During wave packet propagation, the construction of absorption potential can effectively avoid the reflection of wave packet from the grid edge. In this work, the absorption potential along r and R directions is defined as^{11, 12}

$$D(x) = \begin{cases} \exp\left[-\Delta_r \cdot C_a \cdot \left(\frac{x-x_a}{x_b-x_a}\right)^2\right], & x_a \leq x \leq x_b \\ \exp\left[-\Delta_r \cdot C_b \cdot \left(\frac{x-x_b}{x_{\text{end}}-x_b}\right)^2\right] \times \exp(-\Delta_r \cdot C_a), & x_b < x \leq x_{\text{end}} \end{cases} \quad (11)$$

where C_a and C_b define the strength of absorbing potentials, and x_a , x_b , and x_{end} are the positions of absorbing potentials.

Before the wave packet enters the absorption potential region, the reactant-coordinate-based (RCB) method¹³ is employed to perform the transformation from reactant to product Jacobi coordinates. Next, the energy resolved scattering wave function $\psi(E; R_{v_0})$ in the product BF coordinate can be extracted by a Fourier transformation

$$\psi_{v'j'K'}^{Jp}(E; R_{v_0}) = \int_0^{+\infty} e^{iEt} \Psi_{v'j'K'}^{JMp}(t; R_{v_0}) dt \quad (12)$$

The state-to-state scattering matrix element in the product BF representation can be obtained by

$$\psi_{v'j'K' \leftarrow v_0 j_0}^{Jp}(E; R_{v_0}) = -\alpha(E) (2\pi\hbar^2 k_{v'j'} / \mu_R) S_{v'j'K' \leftarrow v_0 j_0}^{Jp}(E) \chi_{l'}(k_{v'j'} R_{v_0}) \quad (13)$$

where $\chi_{l'}$ is an outgoing Riccati-Hankel function. Finally, the reaction probability, integral cross section and differential cross section can be obtained using the S-matrix under the helicity representation.

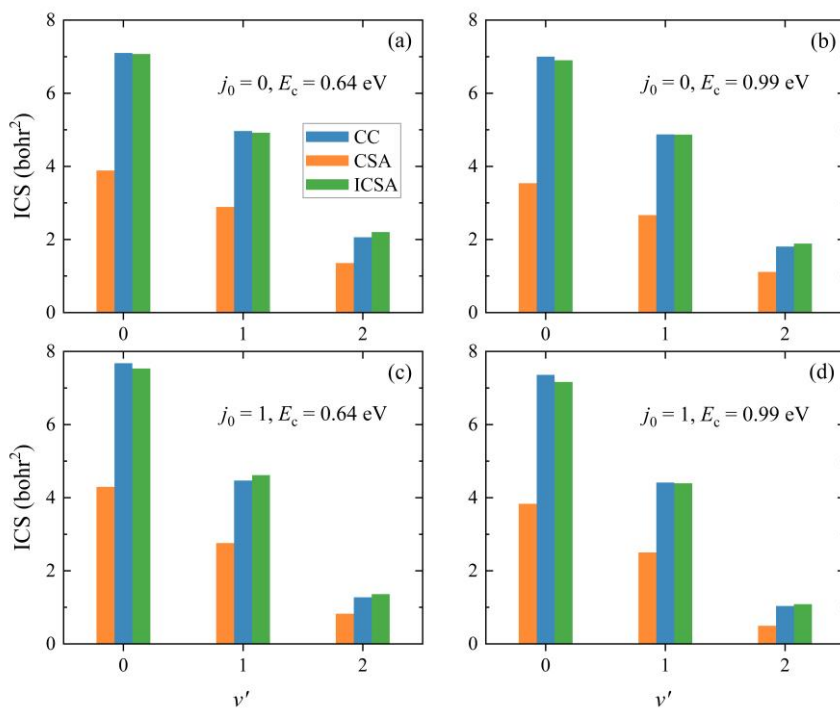


Fig.S1 The product vibration state distribution of $\text{Li}(2p) + \text{H}_2(v_0 = 0, j_0 = 0, 1) \rightarrow \text{H} + \text{LiH}$ reaction at selected collision energies (a, c) $E_c = 0.64$ eV and (b, d) $E_c = 0.99$ eV calculated by the CC, CSA and ICOSA methods.

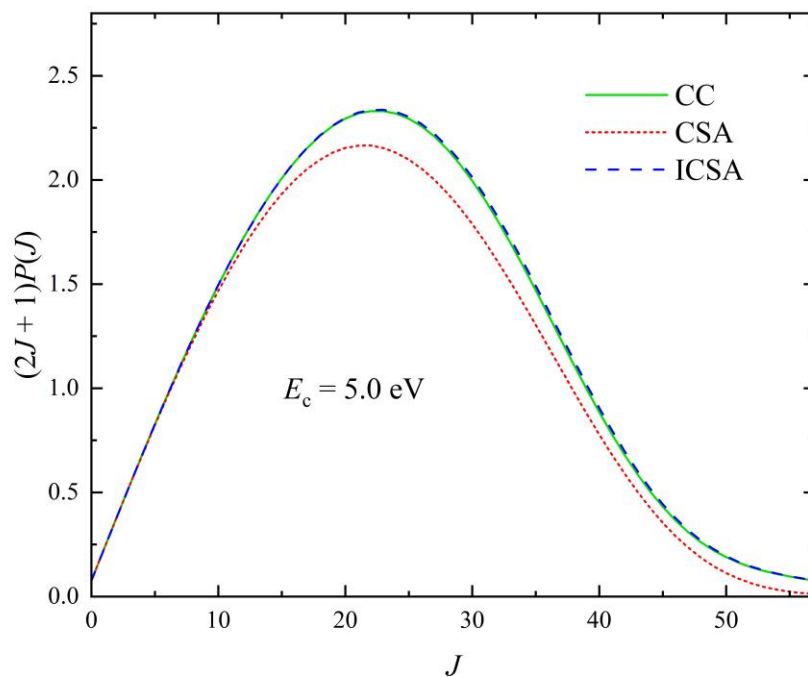


Fig.S2 The opacity functions of the $\text{Mg}^+ + \text{H}_2 (v_0 = 0, j_0 = 0) \rightarrow \text{MgH}^+ + \text{H}$ reaction as the function of total angular momentum J at the selected collision energies $E_c = 5.0$ eV calculated by the CC, CSA and ICSA methods.

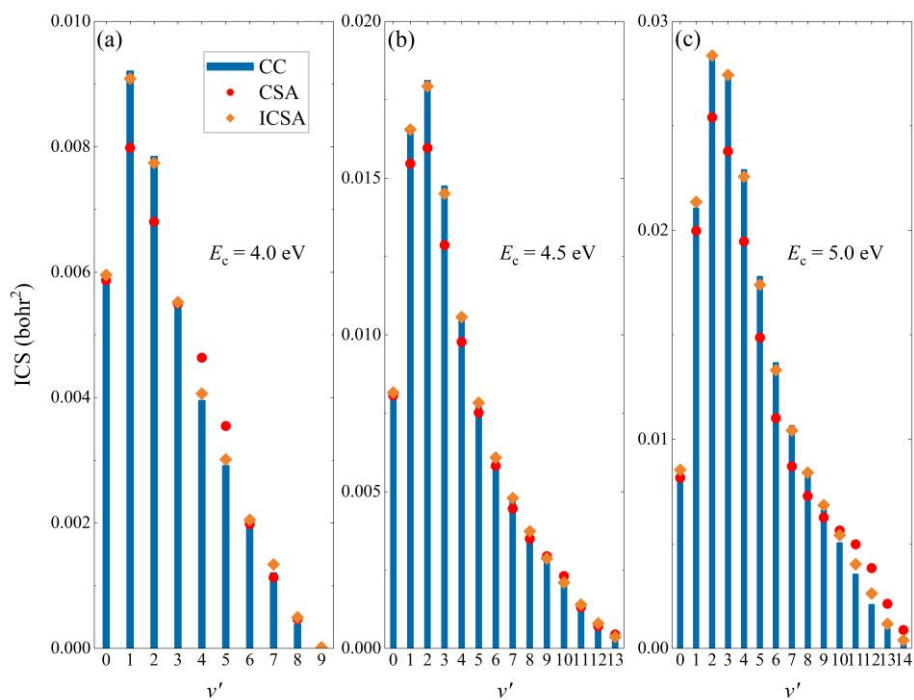


Fig.S3 Comparison of CC, CSA and ICSA methods for the product vibration state distribution of $\text{Mg}^+ + \text{H}_2 (v_0 = 0, j_0 = 0) \rightarrow \text{MgH}^+ + \text{H}$ reaction at selected collision energies (a) $E_c = 4.0$ eV, (b) $E_c = 4.5$ eV and (c) $E_c = 5.0$ eV.

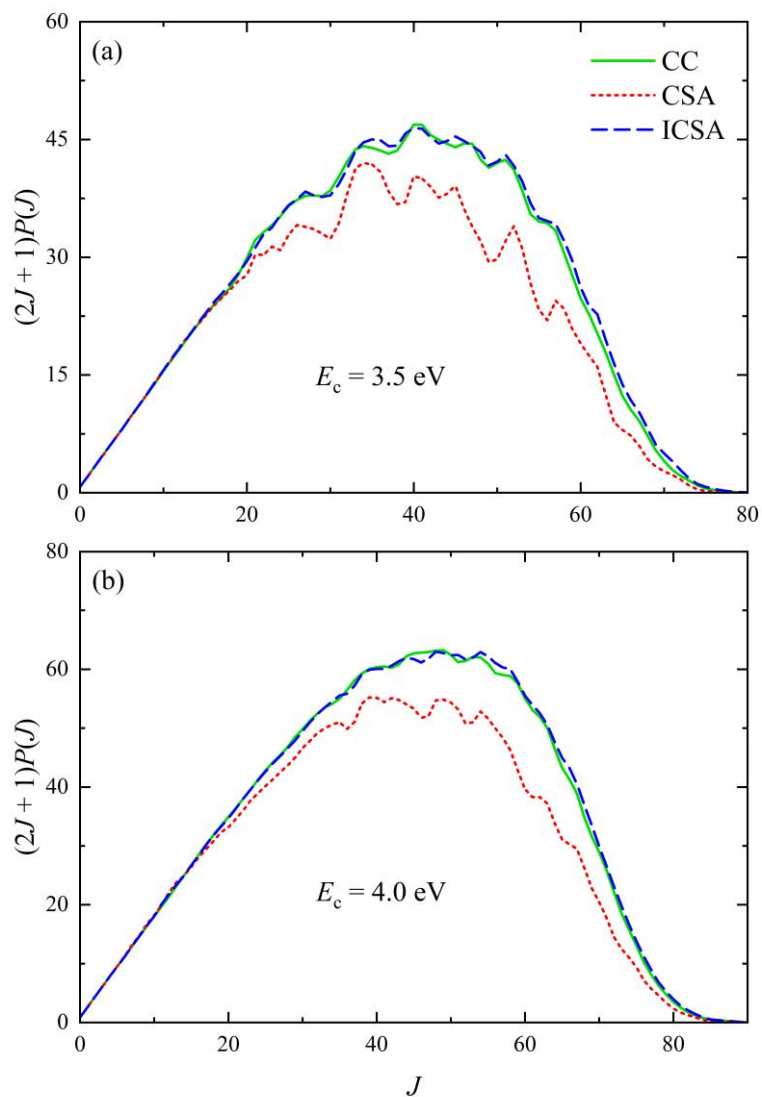


Fig.S4 The opacity functions of the $\text{Ca}^+(^2\text{S}) + \text{H}_2 (v_0 = 0, j_0 = 0) \rightarrow \text{CaH}^+ + \text{H}$ reaction as the function of total angular momentum J at the selected collision energies (a) $E_c = 3.5$ eV and (b) $E_c = 4.0$ eV calculated by the CC, CSA and ICSA methods.

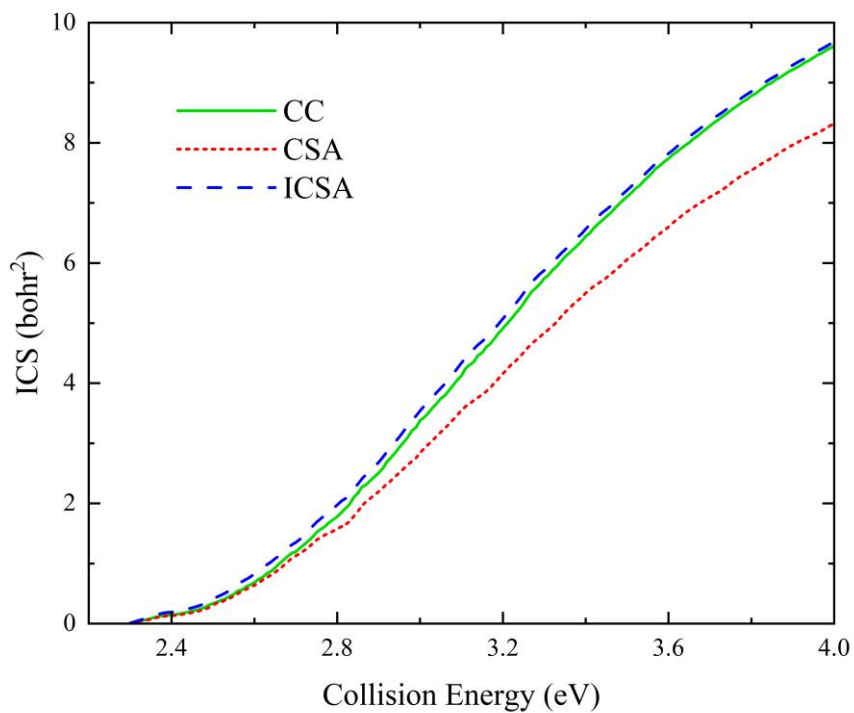


Fig.S5 Comparison of ICSs between the CC, CSA, and ICSA over the collision energy range of 2.2-4.0 eV for the $\text{Ca}^+(^2S) + \text{H}_2 (v_0 = 0, j_0 = 0) \rightarrow \text{CaH}^+ + \text{H}$ reaction.

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