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Fully Coupled ($J > 0$) Time-Dependent Wave-Packet Calculations Using Hyperspherical Coordinates for the H+O_2 Reaction on the CHIPR Potential Energy Surface

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Supplementary Information

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A. Definition of the variables in hypersphrical coordinates:

The definition of the hyperspherical coordinates (ρ, θ, ϕ) in terms of mass-weighted Jacobi coordinates (r, R, γ) can be written as:

$$r_x = -\frac{\rho}{\sqrt{2}}\left(\cos\frac{\theta}{2} + \sin\frac{\theta}{2}\right)\cos\frac{\phi}{2}, \tag{1}$$

$$R_x = \frac{\rho}{\sqrt{2}}\left(\cos\frac{\theta}{2} + \sin\frac{\theta}{2}\right)\sin\frac{\phi}{2}, \tag{2}$$

$$r_y = \frac{\rho}{\sqrt{2}}\left(\cos\frac{\theta}{2} - \sin\frac{\theta}{2}\right)\sin\frac{\phi}{2}, \tag{3}$$

$$R_y = \frac{\rho}{\sqrt{2}}\left(\cos\frac{\theta}{2} - \sin\frac{\theta}{2}\right)\cos\frac{\phi}{2}, \tag{4}$$

$$r_z = R_z = 0, \tag{5}$$

where $\vec{r}$ represents the diatomic vector, $\vec{R}$ denotes the vector connecting the center-of-mass of the diatom to the incoming atom.

The above equations can be further simplified as:

$$r^2 = r_x^2 + r_y^2 = \frac{1}{2}\rho^2(1 + \sin\theta\cos\phi), \tag{6}$$

$$R^2 = R_x^2 + R_y^2 = \frac{1}{2}\rho^2(1 - \sin\theta\cos\phi), \tag{7}$$

$$r^2 + R^2 = \rho^2, \tag{8}$$

and

$$\mathbf{r}\cdot\mathbf{R} = r_x R_x + r_y R_y = -\frac{1}{2}\rho^2\sin\theta\sin\phi. \tag{9}$$

The angle between the $\mathbf{r}$ and $\mathbf{R}$ vectors is known as:

$$\cos\gamma = \frac{\mathbf{r}\cdot\mathbf{R}}{rR} = \frac{-\sin\theta\sin\phi}{\sqrt{1 - \sin^2\theta\cos^2\phi}}, \tag{10}$$

Table 1: Data for initialization, projection, and absorbing potential discussed in the text: H $+O_2$ $(v = 0, j = 1, 3, 5)$

Grid size:	
N_ρ	256
N_θ	64
N_ϕ	128
(ρ_{min}, ρ_{max})/Å	(1.0, 12.0)
Translational wave packet:	
R_0/Å	6.50 ($\sim$ 7.55)[a]
σ/Å	0.21
k_0 (Å^{-1})	29.00772
Initial state:	
E_{vj} (eV)	0.097909
Propagation:	
Δ t (10^{-16} s)	0.50
Magnitude of the five last Lanczos vectors[b]	$10^{-8} - 10^{-7}$
Absorbing potential:	
V_{opt}/eV	0.163
ρ_I (Å)	10.5
Range of the absorbing potential (Å)	10.5 - 12.0
Projection:	
R^* (Å)	3.5 ($\sim$ 4.45)[a]
vib. states	$v' = 0, \cdots, 10$
rot. states	$j' = 0, \cdots, 15$
Maximum Value of Total Angular Momentum:	
J_{max}	45

[a] The transformed values of various parameters in ρ - space are shown in the parenthesis.

[b] All vectors are normalized.

B. Computational Time:

For a particular initial rotational state (j), we require $(2j+1)$ initial components [see Eq. 1 of the main text, where μ denotes the projection of j on the body-fixed Z axis having $(2j+1)$ components]. Their calculation is done once for all during initialization of the wavepacket for a particular run with specific j, v and J. Before the time propagation starts, the initial wavepacket is constructed by summing over all $(2j+1)$ components. The computer times during initialization of the wavepacket are ∼49 min, ∼53 min and ∼58 min for $j = 1$, 3 and 5 states, respectively.

Of course, the initial wavepacket ($\Phi_K(\rho, \theta, \phi)$) depends on K, which is the projection of total angular momentum (J) on the body fixed Z axis having $(2J+1)$ components. As a result, the time dependent Schrödinger equation turns into a set of coupled differential equations for the K-component waves [see Eq. 4]. All calculations are performed using OpenMP parallelization for time propagation by FFT followed by Lanczos iteration. During the use of FFT algorithm and Lanczos iteration, the execution time for each K-component wave depends on J. Additionally, the computational time during projection of the final wavepacket on the asymptotic eigenstates depends on the number of final rotational (j') and vibrational (v') states for the $(J+1)$ number of l' states [see Eq. 6]. Note that the OpenMP parallelization is implemented independently over the three modules (FFT algorithm, Lanczos iteration and projection), while the total execution time is calculated as the sum over times required for those three modules. Figure 1 depicts the execution time with our parallel code as a function of total angular momentum for different initial j states. As shown, the execution time increases almost

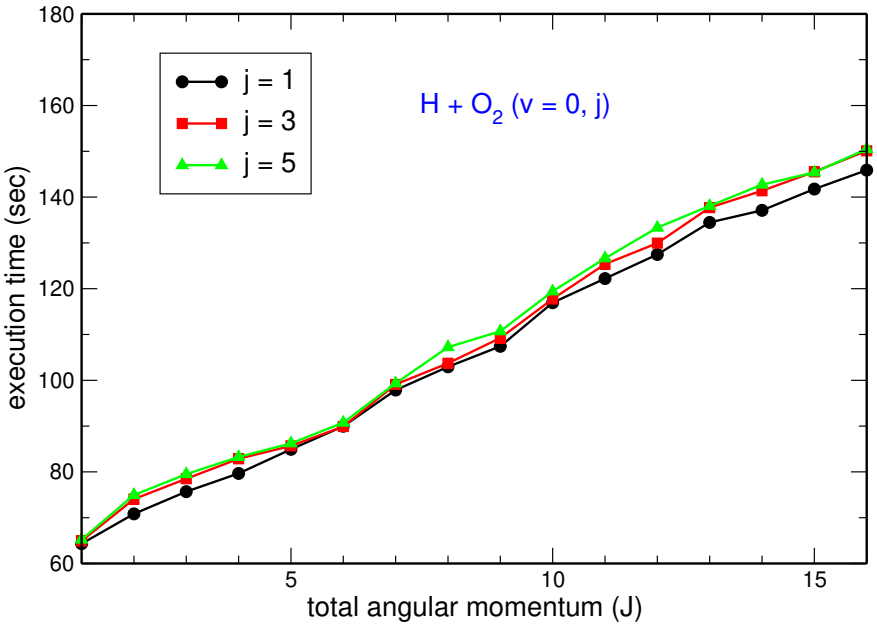

Figure 1: Computational time as a function of total angular momentum for different initial rovibrational states of the diatom with basis set size $256 \times 64 \times 128$.

linearly J, while depicting a negligible effect with increasing j value."