## Supporting Information

*Article*

# Fragment-Based Ab Initio Molecular Dynamics Simulation for Combustion

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### Boundary condition with Jacobi Coordinates

In theoretical chemistry, Jacobi coordinates are usually used to reduce degrees of freedoms in the calculation of polyatomic reactions. For the N-body problem, the Jacobi Coordinates can be written as

$$\boldsymbol{r}_j = \frac{1}{m_{0j}} \sum_{k=1}^{j} m_k \boldsymbol{x}_k - \boldsymbol{x}_{j+1} \; (j = 1,2, \ldots., N-1) \tag{1}$$

$$\boldsymbol{r}_N = \frac{1}{m_{0N}} \sum_{k=1}^{N} m_k \boldsymbol{x}_k \tag{2}$$

$$m_{0j} = \sum_{k=1}^{j} m_k \tag{3}$$

where $\boldsymbol{r}_j$ represents the relative distance between the atom *j+1* and the center of mass of the first *j* atoms; $m_k$ represents the mass of atom *k*; $\boldsymbol{x}_k$ represents the coordinates of atom *k*; $\boldsymbol{r}_N$ represents the coordinate of the center of mass of *N* atoms; $m_{0j}$ represents the total mass of the first *j* atoms.

According to the coordinates, we can derive the velocity

$$\boldsymbol{V}_j = \frac{1}{m_{0j}} \sum_{k=1}^{j} m_k \boldsymbol{v}_k - \boldsymbol{v}_{j+1} \; (j = 1,2, \ldots., N-1) \tag{4}$$

$$\boldsymbol{V}_C = \frac{1}{m_{0N}} \sum_{k=1}^{N} m_k \boldsymbol{v}_k \tag{5}$$

$$m_{0j} = \sum_{k=1}^{j} m_k \tag{6}$$

Correspondingly, $\boldsymbol{V_j}$ represents the relative velocity between the atom *j+1* and the center of mass of the first *j* atoms; $\boldsymbol{v_k}$ represents the velocity of atom *k*; $\boldsymbol{V_C}$ represents the velocity of the center of mass of *N* atoms.

Assume that the initial velocity is a row matrix

$$\boldsymbol{I_k} = [\boldsymbol{v_1}, \boldsymbol{v_2}, \boldsymbol{v_3}, \dots\dots, \boldsymbol{v_k}] \tag{7}$$

It can be converted to Jacobi velocity

$$\begin{bmatrix} \boldsymbol{V_1} \\ \boldsymbol{V_2} \\ \boldsymbol{V_3} \\ . \\ . \\ . \\ \boldsymbol{V_C} \end{bmatrix} = \begin{bmatrix} \mathbf{1} & \frac{\boldsymbol{m_1}}{\boldsymbol{m_1}+\boldsymbol{m_2}} & \frac{-\mathbf{1}}{\boldsymbol{m_1}+\boldsymbol{m_2}} & \mathbf{0} & \dots & \mathbf{0} & \mathbf{0} \\ \frac{\boldsymbol{m_1}}{\boldsymbol{m_1}+\boldsymbol{m_2}+\boldsymbol{m_3}} & \frac{\boldsymbol{m_2}}{\boldsymbol{m_1}+\boldsymbol{m_2}+\boldsymbol{m_3}} & \frac{\boldsymbol{m_3}}{\boldsymbol{m_1}+\boldsymbol{m_2}+\boldsymbol{m_3}} & -\mathbf{1} & \mathbf{0} & \mathbf{0} & \\ \vdots & \vdots & \ddots & & & \vdots & \\ \vdots & \vdots & & \ddots & & \vdots & \\ \frac{\boldsymbol{m_1}}{\sum_{k=1}^{N}\boldsymbol{m_k}} & \frac{\boldsymbol{m_2}}{\sum_{k=1}^{N}\boldsymbol{m_k}} & \dots & \dots & \dots & \frac{\boldsymbol{m_k}}{\sum_{k=1}^{N}\boldsymbol{m_k}} \end{bmatrix} \begin{bmatrix} \boldsymbol{v_1} \\ \boldsymbol{v_2} \\ \boldsymbol{v_3} \\ . \\ . \\ . \\ \boldsymbol{v_k} \end{bmatrix} \tag{8}$$

Formula (8) can be simplified as

$$\boldsymbol{V} = \boldsymbol{A} \times \boldsymbol{I_k^T} \tag{9}$$

We set a matrix

$$\boldsymbol{B} = \begin{bmatrix} \mathbf{1} & \mathbf{0} & \cdots & \cdots & \mathbf{0} \\ \mathbf{0} & \mathbf{1} & \mathbf{0} & \cdots & \mathbf{0} \\ \vdots & \mathbf{0} & \ddots & \mathbf{0} & \vdots \\ \vdots & \vdots & \mathbf{0} & \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \cdots & \cdots & \mathbf{0} & -\mathbf{1} \end{bmatrix} \tag{10}$$

After collision, the velocity of the center of mass is reversed

$$\begin{bmatrix} \boldsymbol{V}_1 \\ \boldsymbol{V}_2 \\ \boldsymbol{V}_3 \\ . \\ . \\ . \\ -\boldsymbol{V}_C \end{bmatrix} = \boldsymbol{B} \times \begin{bmatrix} \boldsymbol{V}_1 \\ \boldsymbol{V}_2 \\ \boldsymbol{V}_3 \\ . \\ . \\ . \\ \boldsymbol{V}_C \end{bmatrix} \tag{11}$$

Then we transform the Jacobi velocicy back to atomic velocities in the Cartesian coordinates.

$$\begin{bmatrix} \boldsymbol{v}'_1 \\ \boldsymbol{v}'_2 \\ \boldsymbol{v}'_3 \\ . \\ . \\ . \\ \boldsymbol{v}'_k \end{bmatrix} = \boldsymbol{A}^{-1} \times \begin{bmatrix} \boldsymbol{V}_1 \\ \boldsymbol{V}_2 \\ \boldsymbol{V}_3 \\ . \\ . \\ . \\ -\boldsymbol{V}_C \end{bmatrix} \tag{12}$$

If we set

$$\boldsymbol{I}'_k = \left[\boldsymbol{v}'_1, \boldsymbol{v}'_2, \boldsymbol{v}'_3, \ldots\ldots, \boldsymbol{v}'_k\right] \tag{13}$$

Formula (12) can be simplified as

$$\boldsymbol{I}'^{T}_k = \boldsymbol{A}^{-1} \times \boldsymbol{B} \times \boldsymbol{A} \times \boldsymbol{I}^{T}_k \tag{14}$$

Finally, we convert the atomic velocity $\boldsymbol{v}_k$ to the velocity $\boldsymbol{v}'_k$ when any atom of the molecule hits the boundary. In this way, the relative atomic velocities and the total kinetic energy of the system remain unchanged.

**Tabel S1.** Reaction energies calculated with MN15 in different basis sets (kcal/mol).

| Reaction | Reaction energies calculated with MN15 in different basis sets (kcal/mol) | | |
|---|---|---|---|
| | 6-31G(d) | 6-31G(d,p) | 6-31G++(d,p) |
| $CH_4 + O_2 \rightarrow CH_3 + HO_2$ | 59.02 | 59.06 | 62.17 |
| $CH_4 + O \rightarrow CH_3 + OH$ | -49.94 | -50.09 | -46.14 |
| $CH_3O \rightarrow CH_2O + H$ | 29.15 | 29.87 | 27.90 |
| $CH_2O + H \rightarrow CHO + H_2$ | -11.27 | -10.63 | -11.61 |
| $CH_2O \rightarrow CHO + H$ | 97.49 | 99.83 | 95.67 |

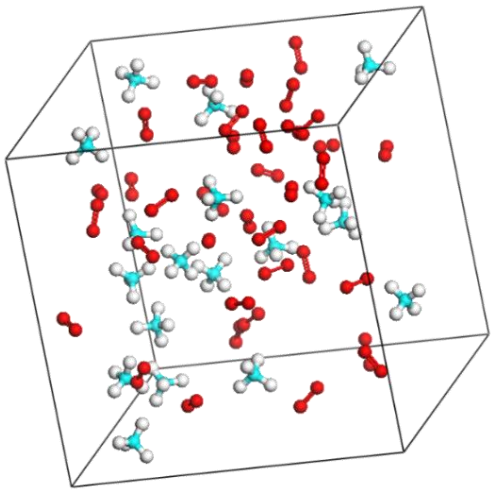

**Figure S1.** The initial structure of the methane-oxygen system.

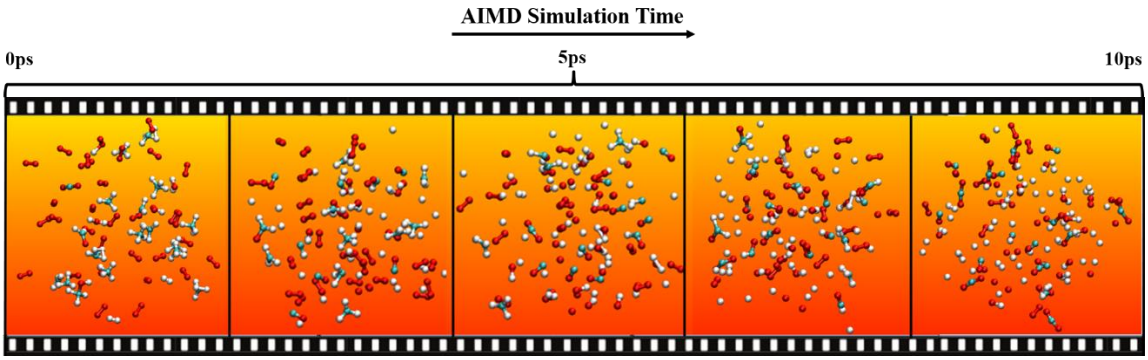


**Figure S2.** Typical snapshots in the FB-AIMD simulation trajectory. The white, cyan-blue, and red balls represent hydrogen, carbon, and oxygen atoms, respectively.

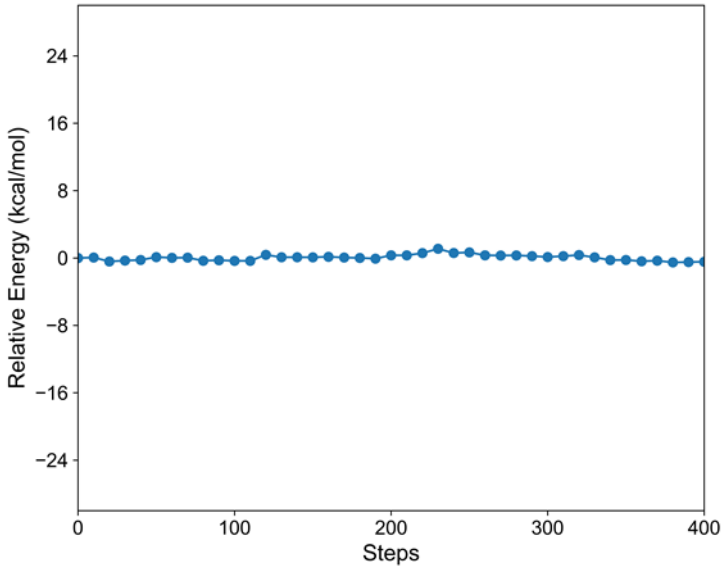


**Figure S3.** The relative total energy of the system during the simulation under the NVE ensemble.