Computational Modeling of a Water Dimer using a TIP3P Model

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Introduction

Objective: Optimize the geometry of water dimer by minimizing the potential energy of the TIP3P model.

Motivation:

- The water dimer is a simple yet essential system for understanding hydrogen bonding.
- TIP3P: A fixed-charge model widely used in molecular simulations.

Potential Energy Function

Expression:

$$E_{ab} = \sum_{i \in a} \sum_{j \in b} \frac{q_i q_j}{r_{ij}} + \frac{A}{r_{OO}^{12}} - \frac{B}{r_{OO}^{6}}.$$

- Electrostatic interactions between partial charges at sites i and j.
- Lennard-Jones potential models short-range repulsion and long-range attraction.
- Parameters A and B are derived from the TIP3P model.

Given Parameters

Parameter	Value
$\angle$HOH	104.5°
r_{OH}	$0.9572\mathring{A}$
q_H	$+0.417$
q_O	-0.834
A	582×10^3 kcal $\mathring{A}^{12}$/mol
B	595 kcal $\mathring{A}^6$/mol

Computational Approach

1. Initialization:
   - Define TIP3P parameters.
   - Set initial values for r_{OO}, α_O, ϕ_O, α_A, and ϕ_A.
2. Energy Calculation:
   - Compute electrostatic and Lennard-Jones contributions.
3. Gradient Descent:
   - Iteratively adjust variables to minimize E_{ab}.

Coordinate System Setup

First Molecule:

- Oxygen at origin $(0, 0, 0)$.
- Hydrogens placed using:

$$r_{\mathrm{OH}}, \quad \angle \mathrm{HOH}.$$

Second Molecule:

- Oxygen position: $\mathbf{r}_{OO} = \{r_{OO}, \phi_O, \alpha_O\}$.
- Hydrogens relative to the second oxygen:

$$\mathbf{r}_{OHA} = \{r_{OH}, \phi_A, \alpha_A\}$$
$$\mathbf{r}_{OHB} = \{r_{OH}, \phi_B, \alpha_B\}$$

Angular Relationship Derivation

Key Constraint: Fixed $\angle$HOH

$$r_{\mathrm{OH}}^2 \cos(\mathrm{HOH}) = \mathbf{r}_{OHA} \cdot \mathbf{r}_{OHB}$$

Substitute vector components:

$$\cos(\mathrm{HOH}) = \sin(\phi_A)\sin(\phi_B)\cos(\alpha_A - \alpha_B) + \cos(\phi_A)\cos(\phi_B)$$

Relationships:

$$\phi_A = \phi_B + \Delta\phi, \quad \alpha_A = \alpha_B + \Delta\alpha$$

Substitute:

$$\cos(\mathrm{HOH}) = \sin(\phi_B)\sin(\phi_B + \Delta\phi)\cos(\Delta\alpha) + \cos(\phi_B)\cos(\phi_B + \Delta\phi)$$

Solving Angular Relationships

Case 1: Let $\phi_B = 0$

$$\cos(\text{HOH}) = \cos(\Delta\phi) \implies \Delta\phi = \text{HOH}$$

Case 2: Let $\phi_B = \frac{\pi}{2}$ and $\Delta\phi = \text{HOH}$

$$\cos(\text{HOH}) = \cos(\text{HOH})\cos(\Delta\alpha)$$

Solve:

$$\cos(\Delta\alpha) = 1 \implies \Delta\alpha = 0$$

Final Relationships:

$$\phi_A = \phi_B + \text{HOH}, \quad \alpha_A = \alpha_B$$

Vector Definitions for Water Molecule System

- **First Molecule:**

$$\mathbf{r_{O1}} = (0,\ 0,\ 0) \qquad \text{(Fixed at origin)}$$

$$\mathbf{r_{H1A}} = r_{OH} \begin{pmatrix} \cos((\pi - thetaHOH)/2) \\ -\sin(\pi - thetaHOH)/2) \\ 0 \end{pmatrix}$$

$$\mathbf{r_{H1B}} = r_{OH} \begin{pmatrix} -\cos((\pi - thetaHOH)/2) \\ -\sin((\pi - thetaHOH)/2) \\ 0 \end{pmatrix}$$

- **Second Molecule:**

$$\mathbf{r_{O2}} = r_{OO} \begin{pmatrix} \sin(\phi_O)\cos(\alpha_O) \\ \sin(\phi_O)\sin(\alpha_O) \\ \cos(\phi_O) \end{pmatrix}$$

$$\mathbf{r_{H2A}} = \mathbf{r_{O2}} + r_{OH} \begin{pmatrix} \sin(\phi_B + \mathrm{HOH})\cos(\alpha_B) \\ \sin(\phi_B + \mathrm{HOH})\sin(\alpha_B) \\ \cos(\phi_B + \mathrm{HOH}) \end{pmatrix}$$

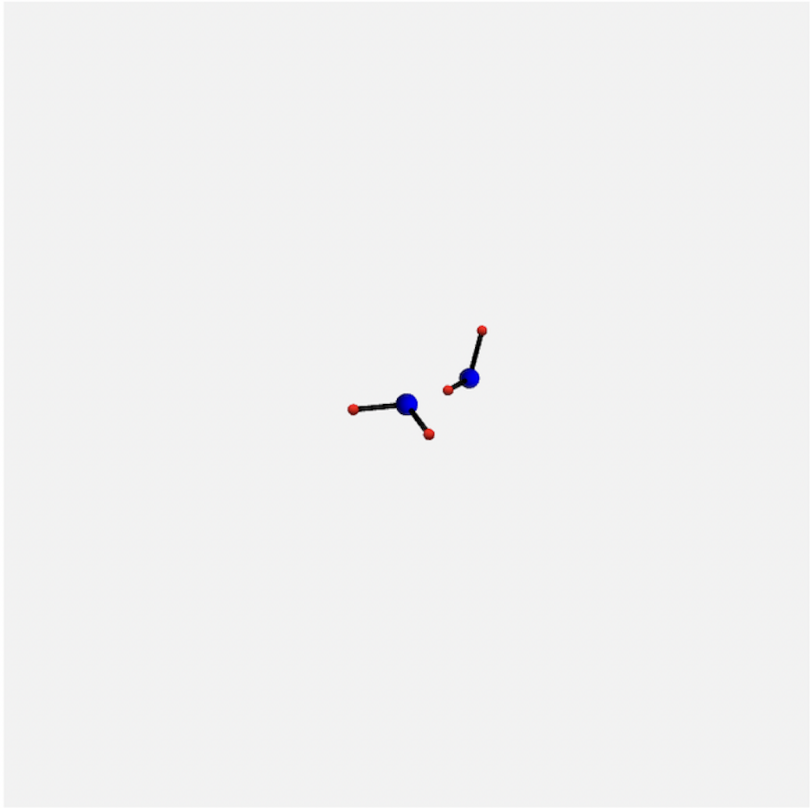
$$\mathbf{r_{H2B}} = \mathbf{r_{O2}} + r_{OH} \begin{pmatrix} \sin(\phi_B)\cos(\alpha_B) \\ \sin(\phi_B)\sin(\alpha_B) \\ \cos(\phi_B) \end{pmatrix}$$

Results

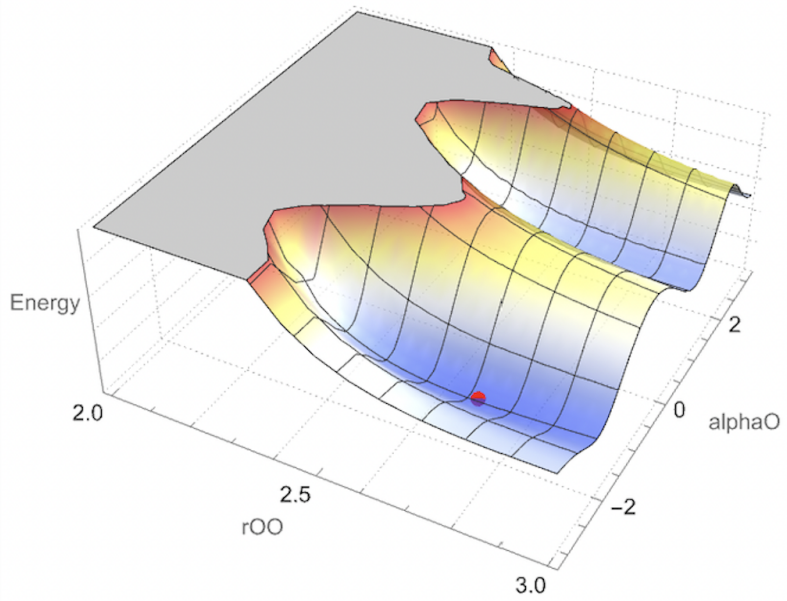
Parameter	Optimized Value
r_{OO} (Å)	2.47
α_O (radians)	-1.95
ϕ_O (radians)	-1.57
α_A (radians)	-0.56
ϕ_A (radians)	-1.57
Energy (kJ/mol)	-6.538

Results

Water Molecule Interaction



Potential Energy Surface



Current Energy(KJ/mol): −6.53805

H-Bond distance: 1.79375

Conclusion

- Successfully modeled the water dimer interaction using a TIP3P framework.
- Identified a stable hydrogen-bonded configuration with a minimum energy of -6.538 kJ/mol.
- Demonstrates the utility of combining computational and visualization tools for studying molecular interactions.