

Ab Initio Molecular Dynamics

Comprehensive Training: Theory and VASP Implementation

Technology Innovation Institute • CMSET 2025, UM6P

Training Overview

Session 1: Introduction to AIMD - This session covers the fundamental principles of Ab Initio Molecular Dynamics, exploring the quantum-mechanical foundations and practical applications in materials science and energy research.

Session 2: Practical Implementation in VASP - Hands-on training focusing on VASP software for Born-Oppenheimer MD, including input file preparation, parameter optimization, and system-specific guidelines for successful simulations.

Target Audience: Researchers and students in computational materials science, chemistry, and physics interested in mastering AIMD techniques for advanced materials characterization and design.

Session 1: Core Concepts

Ab Initio Molecular Dynamics represents the powerful combination of quantum mechanical accuracy with classical molecular dynamics, enabling the study of complex chemical processes with electronic structure fidelity.

This approach bridges multiple scales: quantum mechanics for electronic structure, statistical mechanics for ensemble properties, and classical dynamics for nuclear motion. The fundamental equation governing AIMD is:

$$\underbrace{M_I \ddot{\mathbf{R}}_I}_{\text{Classical Dynamics}} = \underbrace{-\nabla_{\mathbf{R}_I} E_{\text{DFT}}}_{\text{Quantum Forces}}$$

Key AIMD Advantages:

- Quantum Accuracy:** No empirical parameters
- Chemical Reactivity:** Bond breaking/forming
- Electronic Effects:** Polarization, charge transfer
- Predictive Power:** New materials design

Central Question: *How can we efficiently simulate chemical processes while maintaining quantum mechanical accuracy for electronic structure?*

Q Session 1 Major Topics

Fundamental Concepts:

- **What is AIMD?** Quantum forces + Classical dynamics
- **AIMD vs Classical MD** Trade-offs and applications
- **Why AIMD?** Limitations of classical approaches
- **Timescales and Applications** Practical considerations

Technical Approaches:

- **BOMD vs CPMD** Two main flavors compared
- **MD Fundamentals** Ensembles and algorithms
- **Energy Materials** Real-world applications
- **Analysis Methods** From data to knowledge

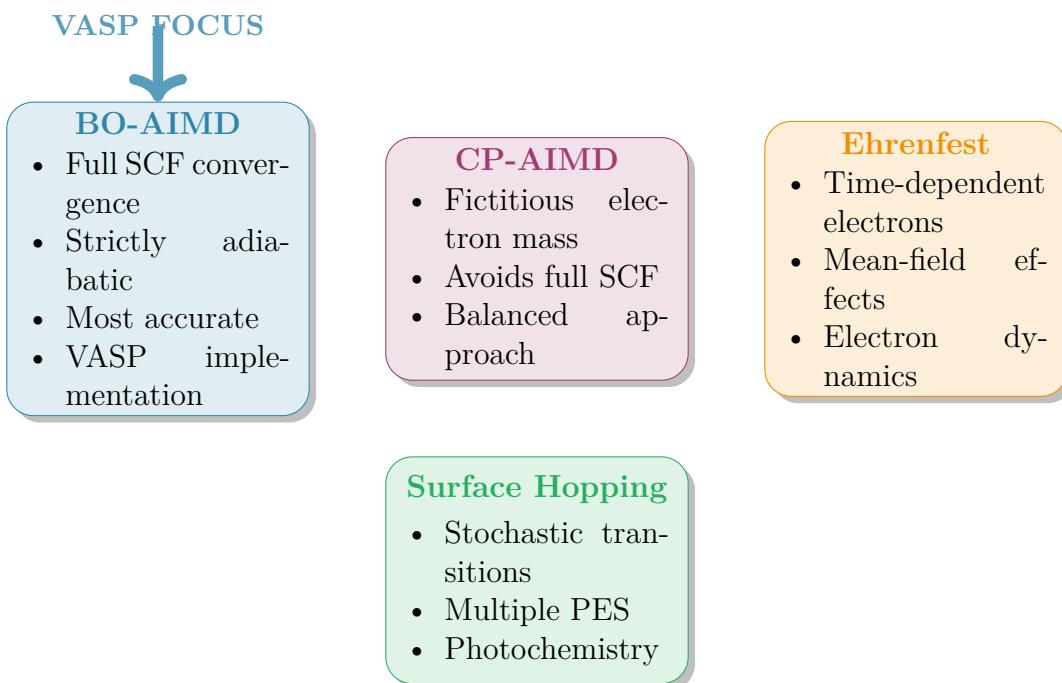
实验室 AIMD Methodologies Compared

Born-Oppenheimer vs Car-Parrinello MD

| Aspect | Born-Oppenheimer MD (BOMD) | Car-Parrinello MD (CPMD) |
|----------------------|--|--|
| Electronic Treatment | <ul style="list-style-type: none"> • Full SCF at each step • Ground state electrons • High accuracy | <ul style="list-style-type: none"> • Extended Lagrangian • Fictitious electron mass • Co-evolving electrons |
| Computational Cost | <ul style="list-style-type: none"> • Expensive per step • Multiple SCF cycles • High accuracy cost | <ul style="list-style-type: none"> • More efficient • No repeated SCF • Faster dynamics |
| Applications | <ul style="list-style-type: none"> • Chemical reactions • Bond breaking • High precision studies | <ul style="list-style-type: none"> • Long trajectories • Efficient sampling • Large systems |

Table 1: Comparison of the two main AIMD approaches and their respective strengths

AIMD Landscape: Four Fundamental Approaches

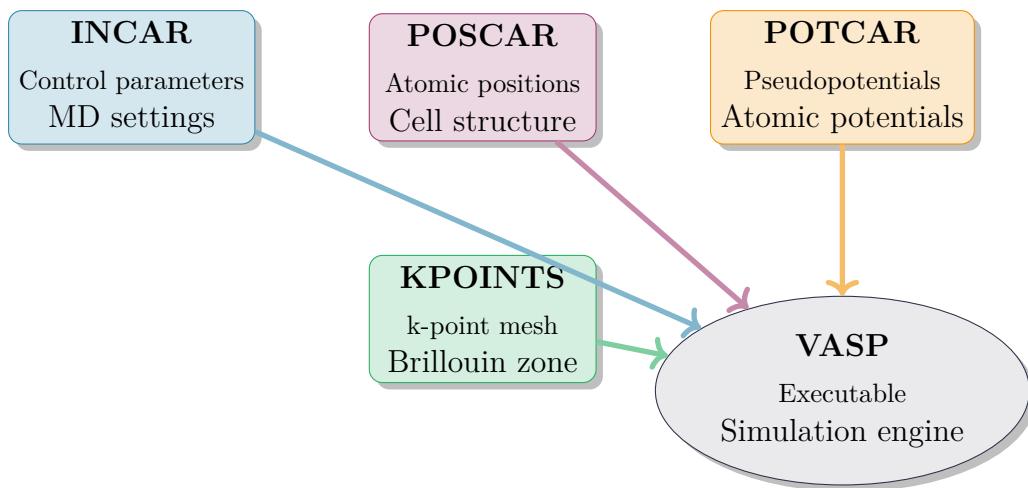


Session 2: VASP Implementation

VASP AIMD Core Philosophy

| VASP Implementation | |
|----------------------|---|
| Feature | |
| Algorithm | Born-Oppenheimer MD (BOMD) with full SCF convergence at each step |
| Activation | IBRION = 0 activates molecular dynamics mode |
| Electronic Structure | DFT-based forces with ground state electrons at every step |
| Performance | LREAL=Auto for efficient real-space projection in MD |
| Limitation | Car-Parrinello MD not implemented in VASP |

VASP Input Files Ecosystem



critical VASP Parameters by Category

| Key Parameters and Settings | |
|-----------------------------|---|
| Category | |
| MD Control | IBRION = 0 (Activate MD) • NSW = 5000 (Number of steps) • POTIM = 1.0 (Time step in fs) • MDALGO = 2 (NVT ensemble) • TEBEG = 300 (Start temperature) • TEEND = 300 (End temperature) |
| Electronic Structure | ISMEAR = 0 (Gaussian smearing) • SIGMA = 0.05 (Smearing width) • ALGO = Fast (MD algorithm) • NELMIN = 4 (Minimum SCF steps) • EDIFF = 1E-5 (SCF accuracy) |
| Performance | LREAL = Auto (Real-space projection) • PREC = Normal (Precision level) • KPAR = 2 (K-point parallelization) • NCORE = 4 (Band parallelization) • LCHARG = .FALSE. (No charge files) • LWAVE = .FALSE. (No wavefunction files) |
| Ensembles | NVE: MDALGO=1, SMASS=-3 • NVT: MDALGO=2, SMASS \geq 0 • NPT: MDALGO=3, PSTRESS=value • Thermostats: Nose-Hoover (accurate) vs Langevin (fast equilibration) |

⚙️ Practical Setup Examples

System-Specific Guidelines

Bulk Crystals

- **Supercell:** $2 \times 2 \times 2$ minimum
- **K-points:** Gamma-point often sufficient
- **Ensemble:** NVT or NPT
- **POTIM:** 1.0-2.0 fs
- **Thermostat:** Nose-Hoover

Liquids & Solutions

- **Cell:** Cubic, 10-15 Å
- **Ensemble:** NPT for density
- **POTIM:** 0.5-1.0 fs
- **Atoms:** 50-200 molecules
- **Thermostat:** Langevin

Surfaces & Interfaces

- **Vacuum:** 15-20 Å minimum
- **Fix layers:** Bottom 2-3
- **K-points:** Dense in plane
- **Dipole corrections**
- **Ensemble:** NVT typical

💻 Theoretical Foundations of MD Analysis Tools

Interatomic Distance Analysis

The distance between two atoms i and j at time t is calculated using the Euclidean distance:

$$d_{ij}(t) = \sqrt{[x_i(t) - x_j(t)]^2 + [y_i(t) - y_j(t)]^2 + [z_i(t) - z_j(t)]^2} \quad (1)$$

Usage:

```
./distance_between_atoms trajectory.xyz
# Select atoms interactively
# Output: distance_1_2.dat (time vs distance)
```

Bond Angle Analysis

The angle θ between three atoms A , B , and C (with B as vertex):

$$\theta_{ABC} = \cos^{-1} \left(\frac{\vec{BA} \cdot \vec{BC}}{|\vec{BA}| |\vec{BC}|} \right) \quad (2)$$

Usage:

```
./angle_between_atoms trajectory.xyz
# Select atom triplets A-B-C
# Output: angle_1_2_3.dat (time vs angle)
```

Mean Squared Displacement and Diffusion

MSD measures spatial extent of random motion:

$$\text{MSD}(t) = \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle \quad (3)$$

Diffusion coefficient from Einstein relation:

$$D = \lim_{t \rightarrow \infty} \frac{\text{MSD}(t)}{2dt} \quad (4)$$

Usage:

```
./xyz_displacement_HJ trajectory.xyz
# Select atoms and dimension (1D/2D/3D)
# Output: displacement_analysis.dat
```

Vibrational Spectrum Analysis

Velocity Autocorrelation Function (VACF):

$$C_{vv}(t) = \langle \vec{v}(0) \cdot \vec{v}(t) \rangle \quad (5)$$

Vibrational Density of States (VDOS):

$$g(\omega) = \int_0^\infty C_{vv}(t) \cos(\omega t) dt \quad (6)$$

Usage:

```
./xyz_vibspec trajectory.xyz
# Select atoms for spectrum calculation
# Output: vibration_spectrum.dat (frequency vs intensity)
```

Temperature Analysis

Instantaneous temperature from equipartition theorem:

$$T(t) = \frac{1}{3Nk_B} \sum_{i=1}^N m_i v_i^2(t) \quad (7)$$

Usage:

```
./temperature_analysis OUTCAR
# Extracts temperature from VASP OUTCAR
# Output: temperature_profile.dat
```

Coordinate System Conversions

VASP direct to Cartesian coordinates:

$$\vec{r}_{\text{cartesian}} = \mathbf{L} \cdot \vec{r}_{\text{direct}} \quad (8)$$

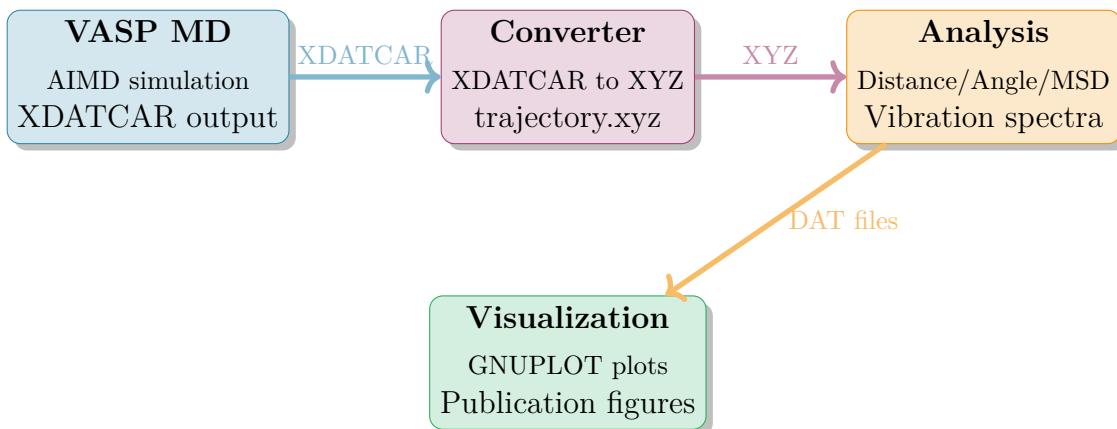
Usage:

```
./robust_xdatcar_to_xyz XDATCAR
# Converts VASP trajectory to XYZ format
# Output: trajectory.xyz
```

</> Analysis Tools Usage Summary

| Tool | Input | Output and Applications |
|--------------|----------------|--|
| Distance | XYZ trajectory | <ul style="list-style-type: none"> Bond length fluctuations Intermolecular distances Hydrogen bonding analysis |
| Angle | XYZ trajectory | <ul style="list-style-type: none"> Bond angle distributions Molecular geometry Torsion angles |
| Displacement | XYZ trajectory | <ul style="list-style-type: none"> Diffusion coefficients MSD/RMSD analysis Mobility studies |
| Vibration | XYZ trajectory | <ul style="list-style-type: none"> Vibrational spectra Phonon density of states Bond vibrations |
| Temperature | VASP OUTCAR | <ul style="list-style-type: none"> Temperature profiles Thermostat performance Ensemble validation |
| Converter | VASP XDATCAR | <ul style="list-style-type: none"> XYZ format trajectories Cross-platform compatibility Visualization preparation |

⚙️ Complete Analysis Workflow



💡 Key Takeaways and Best Practices

Session 1 Summary: AIMD combines quantum mechanical accuracy with molecular dynamics, enabling the study of chemical reactions and electronic effects. The trade-off between system size/simulation time and electronic accuracy/chemical reactivity defines practical applications.

Session 2 Summary: VASP implements Born-Oppenheimer MD with full SCF convergence at each step. Proper setup of INCAR parameters, ensemble selection, and system-specific guidelines are crucial for successful simulations. Always test with short runs (NSW=100) before production.

Best Practices: Start from relaxed structures • Test POTIM for energy conservation • Use appropriate ensembles (NVT for solids, NPT for liquids) • Monitor OSZICAR for simulation health • Validate with experimental conditions when possible.

💡 Practical Exercises

Exercise Series: The following exercises are designed to build comprehensive AIMD skills through practical implementation and analysis of molecular systems.

Exercise 1: NVT AIMD for Phenol-Water System

| Task | Analysis Objectives |
|-----------------------------|---|
| System Setup | <ul style="list-style-type: none">• Create simulation box with 1 phenol molecule + 32 water molecules• Use cubic box $5 \times 15 \times 5 \text{ \AA}$ for 1 g/cm^3 density• NVT ensemble at 300 K with Nose-Hoover thermostat |
| Temperature Analysis | <ul style="list-style-type: none">• Plot Temperature vs Time from OUTCAR• Verify thermostat stability ($\pm 10 \text{ K}$ fluctuations acceptable)• Calculate average temperature over production run |
| Distance Analysis | <ul style="list-style-type: none">• Calculate O(phenol)-O(water) distance vs time• Identify hydrogen bonding patterns• Analyze solvation shell structure |
| Diffusion Analysis | <ul style="list-style-type: none">• Compute MSD for entire system• Separate MSD for water molecules only• Separate MSD for phenol molecule only• Calculate diffusion coefficients from linear MSD regime |

Exercise 2: NVE Ensemble Validation

| Task | Validation Objectives |
|------------------------|--|
| System Setup | <ul style="list-style-type: none">• Use final configuration from NVT run as starting point• Switch to NVE ensemble (microcanonical)• Run for 2-3 ps to check energy conservation |
| Energy Analysis | <ul style="list-style-type: none">• Monitor total energy conservation in OSZICAR• Check temperature drift (should be minimal)• Analyze potential vs kinetic energy exchange |
| Validation | <ul style="list-style-type: none">• Verify proper thermalization from NVT run• Confirm time step (POTIM) appropriateness• Validate force accuracy and SCF convergence |

Exercise 3: NPT AIMD for Phenol-Water System

| Task | Analysis Objectives |
|----------------------------|--|
| System Setup | <ul style="list-style-type: none">• Same phenol-water system as Exercise 1• Switch to NPT ensemble at 300 K and 1 bar• Allow box size fluctuations |
| Density Analysis | <ul style="list-style-type: none">• Monitor box volume vs time• Calculate instantaneous density• Compare with experimental water density (0.997 g/cm³ at 25°C) |
| Structural Analysis | <ul style="list-style-type: none">• Compare O(phenol)-O(water) distances with NVT results• Analyze any density-dependent structural changes• Calculate radial distribution functions |
| Comparison | <ul style="list-style-type: none">• Contrast diffusion coefficients between NVT and NPT• Compare hydrogen bonding lifetimes• Analyze ensemble effects on solvation structure |

Exercise 4: Bulk Water System Analysis

| Task | Analysis Objectives |
|------------------------------|---|
| System Setup | <ul style="list-style-type: none"> • Create bulk water system with 64 HO molecules • Adjust box size for target density 0.99 g/cm^3 • Use NPT ensemble to relax to experimental density |
| Polarization Analysis | <ul style="list-style-type: none"> • Calculate H(water)-O(neighbor) distance vs time • Analyze hydrogen bond network dynamics • Study dipole moment fluctuations |
| Diffusion Analysis | <ul style="list-style-type: none"> • Compute MSD for oxygen atoms only • Compute MSD for entire system • Calculate water self-diffusion coefficient • Compare with experimental value ($2.3 \times 10 \text{ cm}^2/\text{s}$ at 25°C) |
| Hydrogen Bonding | <ul style="list-style-type: none"> • Track H-O distances between molecules • Analyze hydrogen bond lifetimes • Calculate coordination numbers |

Analysis Tools for Exercises

Temperature Analysis

```
./temperature_analysis  
From OUTCAR
```

Distance Analysis

```
./distance_between_atoms  
O-O, H-O distances
```

Diffusion Analysis

```
./xyz_displacement_HJ  
MSD and D
```

Trajectory Conversion

```
./robust_xdatcar_to_xyz  
XDATCAR to XYZ
```

Expected Outcomes:

- **Exercise 1:** Understanding of NVT ensemble behavior, phenol solvation structure, and component-specific diffusion
- **Exercise 2:** Validation of proper thermalization and energy conservation in MD simulations
- **Exercise 3:** Comparison of NVT vs NPT ensemble effects on structure and dynamics
- **Exercise 4:** Comprehensive analysis of bulk water properties including polarization, diffusion, and hydrogen bonding