Atomistic & Molecular Simulations

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Atomistic Technology of Materials (ATOM) Software Suite for Computing Properties of Molecules and Materials

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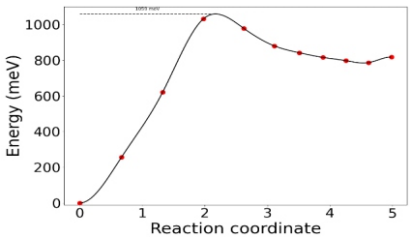

Activation barrier for Hydrogen on Metal Lattice

ABSTRACT

The ATOM (Atomistic Technology of Materials) initiative aims to develop a user-friendly software suite dedicated to streamlining input, output, and analysis for atomistic and molecular simulations. This letter focuses on the design and development of a sub module of ATOM software, specifically developed for calculations pertaining to the "Gas Storage and Permeation". Implemented using Python and the Django web framework, the application empowers users with functionalities such as job registration, viewing and editing existing jobs, file uploads and processing, and comprehensive analysis of calculated data. Through this platform, users can delve into diverse data sets, including energies, absorption energy, hydrogen gas diffusion, permeation, and solubility, enabling a thorough analysis. With a meticulously designed database schema, the application efficiently organizes and stores critical job-related information, files, energy profiles, parameters, and frequencies. Overall, this application stands as a valuable resource, offering both a user-friendly interface and robust analytical tools for managing and examining atomistic simulation data. Its significance lies in its potential to greatly benefit researchers operating in the fields of materials science and chemistry.

KEYWORDS: *Atomistic modelling, DFT, Molecular Dynamics, SX and IX, Multi-component Glass, Barrier materials*

Introduction

The recent advancements in computational chemistry and materials modeling along with computing technologies paved the way for design and development of novel materials with finest properties. Several material modeling software are presently available under open and private licenses. For example, the open software for material modeling includes GROMACS[1], LAMMPS [2], QUANTUM Espresso [3], etc. and private license software include TURBOMOLE [4], SCM-ADF [5], VASP [6], QUANTUM-ATK [7], etc. Each software has their own application and limitations for predicting the atomistic/ molecular system and a single software cannot serve all the purpose. Hence, there is an urgent requirement for indigenous development of a software suite which can prepare the input, analyze and visualize the output and predict the molecular properties and work across all these types of software. Further, the computing solutions are very much required for visualization of properties of materials, the visualization will enhance the molecular study of various materials and will seed the next generation products to meet out the industrial requirements. The visualization technique is significant in bringing hidden physical properties of the material. The popular GUI are VMD [8], MERCURY [9], VESTA [10] etc. The main objective of ATOM software is to develop an Indigenous Integrated Environment which is capable of accepting the output of various atomistic simulation software and to extract meaningful information to further provide more complex insights of the atomistic world. To design and develop this software it has been divided into six software modules which cater to following application areas: (i) Ion Extraction, Adsorption and Isotope separation, (ii) Gas Storage and Permeation, (iii) Water Purification and Desalination, (iv) Reaction Mechanism and Catalysis, (v) Multicomponent Glass, (vi) Energy Materials.

The present report describes the development and implementation of a software module for analyzing and managing atomistic simulation data for gas storage and permeation. This module is developed to analyze the material for gas storage (e.g., H_2) and permeation of gas through metals.

Chemistry of Gas Storage and Permeation

In a dense metallic membrane, hydrogen permeation occurs in seven steps as shown Fig.1, which are

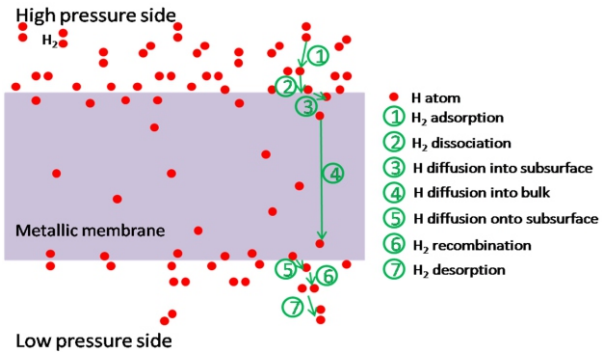

Fig.1: Schematic diagram of Hydrogen permeation through metal.

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- Adsorption of H_2 molecule at the high pressure side of the membrane surface.
- Dissociation of H_2 on the membrane surface.
- Penetration of H from surface to membrane bulk.
- Diffusion of H through the membrane bulk,
- Diffusion of H from membrane bulk to the surface on the collector side (low pressure) of the membrane,
- Recombination of H_2 molecule on the membrane surface.
- Desorption of H_2 from the collector side surface of the membrane.

Absorption or Adsorption Energies of H Isotopes in Bulk Metal or Surface

The absorption energy H atom in the bulk metal can be written as:

$$E_{ab} = E_{MnH} - E_{mn} - \tfrac{1}{2} E_{H2}$$

Here $E_{(MnH)}$ represents the energy of H atom in bulk supercell with n metal atoms. $E_{(Mn)}$ represents the energy of bulk supercell with n metal atoms.

The zero point energy (ZPE): $ZPE = \sum_i \frac{(h\nu_i)}{2}$

Diffusion of H and its Isotopes in the Surface/Bulk

Using harmonic transition-state theory in the classical limit and the random-walk model of interstitial diffusion in a lattice.

$$D = D_0 \exp^{\frac{-[\Delta E_a]}{kT}}$$

D_0 in the Arrhenius expression for the temperature-dependence of the diffusion constant D can be expressed as:

$$D_0 = \frac{n}{6} a^2 \frac{\prod_{j=1}^{3N} \vartheta_j}{\prod_{j=1}^{3N-1} \vartheta\#_j}$$

Here, n is a geometrical factor for the number of equivalent jump paths (4 for H in the T-site), a is the jump length, and ϑ_j and $\vartheta\#_j$ are the real normal mode frequencies at the initial state and the transition state, respectively.

The zero-point energy correction to barrier height can be considered using harmonic vibration frequencies and at room temperature.

$$E_a = E_{TS} - E_{stable} \qquad \Delta ZPE_a = ZPE_{TS} - ZPE_{stable}$$

Permeation and Solubility

The permeability (Θ) can be evaluated using:

$$\Theta = \tfrac{1}{2} K_s(T)\, D$$

$K_s(T)$ and D is the Sieverts constant (solubility) and diffusivity.

$$K_s(T) = exp\left(\beta\left[\sum_i \frac{h\omega_i}{4} - E_b - \sum_i \frac{h\vartheta_i}{4}\right]\right) \frac{1}{\sqrt{\alpha}} \{\sqrt{(1 - exp[-\beta \sum_i \frac{h\omega_i}{2}])}\} \frac{1}{\prod_i (1 - exp(-\beta(h\vartheta_i)))}$$

with

$$\alpha = \left[\frac{2\pi mkT}{h^2}\right]^{\frac{3}{2}} \left\{\frac{4\pi^2 I(kT)^2}{h^2}\right\} \qquad \beta = \frac{1}{kT}$$

ωi am and ϑi correspond to the vibrational frequency of isolated H_2 molecule and H atom in bulk metal. E_b is the binding energy of H atom with bulk metal. 'm' and 'I' represent the mass and moment of inertia of H_2 molecule. k, T and h are the Boltzmann constant, temperature and Planck's constant respectively. The atomistic simulations were performed using VASP and initial input was prepared using VNL.

Design and Development of Gas Storage and Permeation Module

The objective of Gas Storage and Permeation module is to calculate absorption or adsorption energies, diffusion, permeation and solubility constants of H and its isotopes in the metal surface or bulk. To achieve these goals, this module performs following three major tasks: (i) extraction of valuable information from the output files of various atomistic simulation software and to store them in the database., (ii) processing of the primitive data stored in database to compute more specific information related to "Gas Storage and Permeation", and (iii) a web based GUI to facilitate users to perform various operations such as uploading output files, data visualization and downloading generated results in form of excel sheets and plots.

Extraction of Important Data

This software module extracts the primitive information from the uploaded output files viz. OUTCAR, OSZICAR, CONTCAR etc., pertaining to structural optimization, single point and frequency calculations and folders from the Nudge Elastic Band (NEB) calculations using VASP software. This extracted information is stored in the database and uploaded files are stored against each job on the predefined area on the application server.

The module retrieves a list of all unprocessed job files from the database that are currently not being processed. Then, for each job file in the list, it retrieves, processes, and stores the information from job files in the database, ensuring that only unprocessed jobs that are not already being processed are processed. The first step is to set the jog state to "is_processing" and then procced with the processing. The job state is used to keep track of which jobs are currently being processed. If the file type is "OTC", "OTCI" or "OTCT", the function first reads the vibrational frequencies from the file, and calculates the zero-point energy (ZPE). It then saves the ZPE value to the database. It also saves the real and imaginary frequencies to the database as separate instances of the JobFreq model. If the file type is "TAR" or "ZIP", it first extracts the contents of the file (either tar or zip). The file is first extracted to a directory using either the zip file or tarfile libraries, followed by NEB analysis. It then calculates the initial energy, transition energy, transition index, and distance. These values are saved to the database using the JobParams and JobEnergies database models. Finally, the script generates a plot of the data and saves it before removing the extracted directory. Once all the processing is complete, the function marks the job as completed.

Computation of Absorption Energy, Diffusion, Permeation and Solubility of Gas

This module computes values of various coefficients and constants required for generating equations for gas diffusion, permeation and solubility. First, it computes corrected Absorption Energy with zero point correction. This amount energy is released by placing a H atom in the metal lattice. Second, it calculates gas diffusion coefficient and temperature dependent plots for the chosen range. Diffusion coefficient provide insights of thermal motion of gas particles through metal lattice. Next is calculation of solubility constant (Ks), alpha, beta and graphs of solubility constant against temperature. These are used in determining volume of gas that can be dissolved in a unit volume of metal. Solubility constant (Ks) is further used in calculation of permeation coefficient which provides estimates of penetration of gas through solid. This module also computes Thermal desorption spectrum

(TDS) of gas on the metal surface. Thermal desorption spectrum is simulated using AIMD simulations and Polanyi–Wigner equation to understand surface desorption kinetics. This module takes various inputs provided by the user such as participating molecules, order, gas coverage, pre-factor and starting and ending temperature. Then solves the Polanyi–Wigner equation using numerical method and plots the thermal desorption spectrum. Computed data and plots are archived for future reference.

Web based Graphical User Interface (GUI)

The graphical user interface facilitates users to use the application. It was decided to develop a web-based GUI instead of standalone (desktop based) application due its advantages over the later. Web based applications can be accessed over the network using browsers without requiring any installation at user end. These applications can be developed and updated efficiently and have wider reachability as they are independent of client machine's operating system. Following is the description of the various sections of ATOM web interface:

Login

This is the first page where user lands on accessing https://atom.megh.barc.gov.in through its web browser. Here, a registered ATOM user can login using the ATOM credentials. In case, a user forgets the password, a reset link is sent to his BARC email which enables it to change the password.

Register Job

This section allows users to submit a new job to the application. As per ATOM's nomenclature, a job is any simulation run whose output files are to be uploaded to ATOM for further processing. It has a form containing job name, molecule, job type, and job description fields. The molecule field is a small WYSIWYG editor in which users can add subscripts and superscripts. The job type is a drop-down field with the following options: Optimization Run, Optimization Run (Metal), and NEB. The frontend and backend validations are done before saving the job to the database. When a job is registered successfully, the user is redirected to a job list page, and a message is displayed confirming that the job has been registered. If there are any errors in the form, error messages are displayed to the user.

Job List and Update Job

Job list section contains a list of all the jobs registered by the user. The pagination is used to restrict the number of jobs to 10 per page. It contains the job name, molecule, job type, job status, and job creation date. It allows the user to delete the job and contains links to update the job, manage the job files, and show job energies. A job has the following status: Calculated, Ready to calculate, Calculating, Missing files, and Invalid files.

Update Job section allows users to update an existing job. It contains a form containing job name, molecule and job description fields. The molecule field is a small WYSIWYG editor in which users can add subscripts and superscripts. The frontend and backend validations are done before saving the job to the database. When a job is successfully updated, the user is redirected to a job list page, and a message is displayed confirming that the job has been updated. If there are any errors in the form, error messages are displayed to the user.

Manage Files

This section allows users to upload and view files associated with a specific job. If the job type is Optimization Run, then the form requires the user to upload OSZICAR and OUTCAR files.

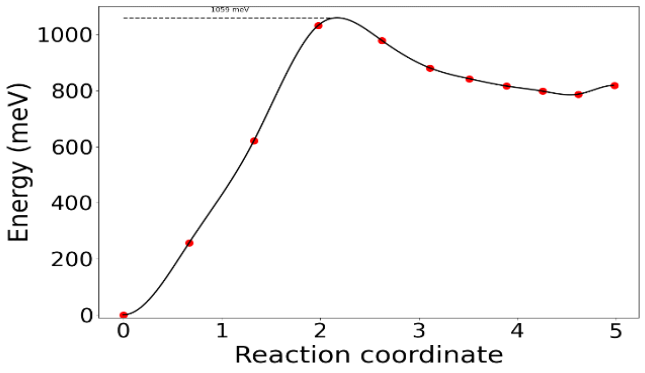
If the job type is Optimization Run (Metal), then the form requires the user to upload only an OSZICAR file. If the job type is NEB, then the form initially requires the user to upload a zip or tar file and the number of similar nearest neighbours. Once the uploaded file is processed, the user is given the index of the initial and transition states and is required to upload the respective OUTCAR files. As the files may be large, the user is shown a progress bar while the file is being uploaded. After the file is uploaded, the user is given the option to delete the file. If the file is being processed, the delete button is disabled. If the uploaded files are found to be invalid during processing, the user is notified and given the option to replace the file. The view also contains a link to the "Show Energies" section of the correlating job.

Show Energies

This section contains the job name, job type, molecule, job description, and job status. If the job status is "Calculated," the different parameters related to the job are displayed. If the job status is "Ready to Calculate," a "Calculate Now" button is displayed, which a user may click to process the job files; otherwise, the job files are automatically processed by the cron jobs. If the job status is "Calculating," a disabled button is

Show Energies

Job Name	Fe-H-0.5ML-desorption
Job Type	NEB
Molecule	$Fe_{20}H_2$
Description	Desorption run for TDS
Job Status	Energy has been calculated.



Initial ZPE	0.0575 eV
Activation ZPE	0.0931 eV
ZPE Correction	0.0356 eV
Activation Energy	1059.4431 meV
Corrected Activation Energy	1.095 eV
Distance	4.9793 A
Stable Image Index	0
Transition Image Index	3
Similar Nearest Neighbours	1
Real Frequencies (Initial)	51.7107 meV, 34.0341 meV, 29.2431 meV
Imaginary Frequencies (Initial)	13.7682 meV
Real Frequencies (Transition)	75.2256 meV, 73.7888 meV, 37.1435 meV
Imaginary Frequencies (Transition)	36.7213 meV
D_0	0.0 cm^2/s

Fig.2: Show Energies page showing various job data.

displayed to indicate that the job files are being processed. If the user has not uploaded all the files, an "Upload Files" button linking to "Manage Files" is displayed. If the uploaded files are invalid, a "Replace Files" button linking to "Manage Files" is displayed.

Absorption Energy

This section is used to calculate the absorption energy. Firstly, the user is presented with a form to enter the number of reactants and products. After submitting the form, the form details are validated at the frontend and backend. If the form is valid, the user is presented with a form to select reactants and products using a drop-down menu and their respective coefficients, and a button to calculate the energy. The menu contains all the Optimization Run and Optimization Run (Metal) jobs, with only the jobs whose parameters are already processed. After clicking the "Calculate Energy" button, the form is again validated at the front and back ends, and if the form is valid, the equation along with absorption energy, ZPE correction, and corrected absorption energy are displayed.

Gas Diffusion

This section is used to calculate the gas diffusion rate over a range of temperatures. The user is presented with a form that contains a dropdown to select the NEB job (with only calculated jobs enabled) and fields for entering the starting temperature, ending temperature, step size, and multiplication factor. The user is also given a button that triggers a script that validates the data, generates various graphs, and calculates various parameters. The generated graphs and calculated parameters are shown to the user, and the user is given the option to download the graphs and the csv files containing the calculated parameters and graph coordinates.

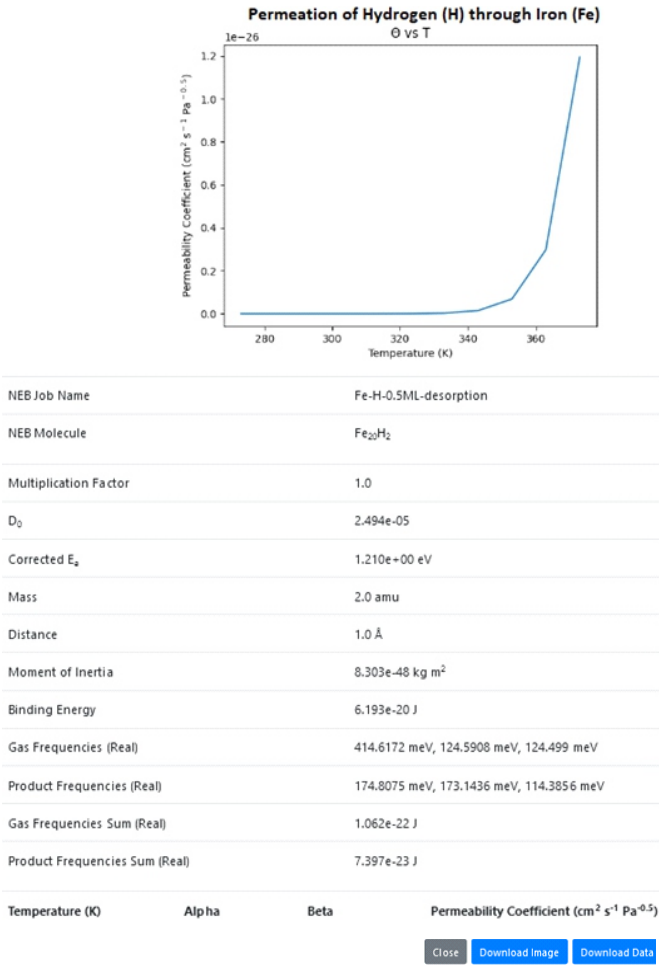


Fig.3: Permeation of Hydrogen in Iron computed using ATOM.

Gas Solubility

This section is used to calculate the gas solubility rate over a range of temperatures. The user is presented with a form containing an equation with fields for choosing a metal reactant from the dropdown containing Optimization Run (Metal) jobs, a gas reactant from the dropdown containing Optimization Run jobs, and a metal hydride product from the dropdown containing Optimization Run jobs. The form also contains fields for entering the starting temperature, ending temperature, step size, atomic mass, and distance. The user is also given a button that triggers a script that validates the data, generates various graphs, and calculates various parameters. The generated graphs and calculated parameters are shown to the user, and the user is given the option to download the graphs and the csv files containing the calculated parameters and graph coordinates.

Gas Permeation

This section is used to calculate the gas permeation rate over a range of temperatures. The user is presented with a form containing an equation with fields for choosing a metal reactant from the dropdown containing Optimization Run (Metal) jobs, a gas reactant from the dropdown containing Optimization Run jobs, and a metal hydride product from the dropdown containing Optimization Run jobs. The form also contains a drop-down to select the NEB job and fields for entering starting temperature, ending temperature, step size, atomic mass, distance, and multiplication factor. The user is also given a button that triggers a script that validates the data, generates various graphs, and calculates various parameters. The generated graphs and calculated parameters are shown to the user, and the user is given the option to download the graphs and the csv files containing the calculated parameters and graph coordinates.

Conclusion

The ATOM (Atomistic Technology of Materials) represents an integrated module engineered to enhance the management of input, output, and analysis processes for atomistic and molecular simulations. Embedded within the ATOM Graphical User Interface (GUI) are four distinct sub-modules, each offering a suite of comprehensive tools. This report specifically outlines the development and deployment of a web application dedicated to the analysis and administration of atomistic simulation data, focusing on the Gas Storage and Permeation sub-module. In conclusion, the Gas Storage and Permeation module serves as a vital tool for researchers in materials science and chemistry, offering a comprehensive solution for analyzing atomistic simulation data. With its focus on calculating absorption energies, diffusion, permeation, and solubility constants of hydrogen and its isotopes in metal surfaces or bulk materials, this module plays a crucial role in advancing understanding in these fields. Through its intuitive web-based interface, users can efficiently manage input and output files, visualize data, and access results in formats suitable for further analysis. Overall, the Gas Storage and Permeation module stands as an indispensable asset, empowering researchers with the tools they need to conduct in-depth analysis and drive progress in atomistic research.

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