Potential Energy Surface Scan of n-butane Using Various Quantum Chemistry Software

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Abstract

A potential energy surface (PES) scan is central to numerous problems in quantum chemistry, including identifying reaction mechanisms, reaction kinetics, transition states, activation barrier, etc. This work details the potential energy surface scan of the dihedral angle of the molecule n-butane using various open-source/freeware computational quantum chemistry software, including CP2K, GAMESS, NWChem, ORCA, Psi4, and PySCF. The input preparation, adopted methodology, execution flow, and results are discussed in detail, equipping readers with the necessary hands-on knowledge of computational tools to perform electronic structure calculations through a dihedral scan.

Graphical Abstract

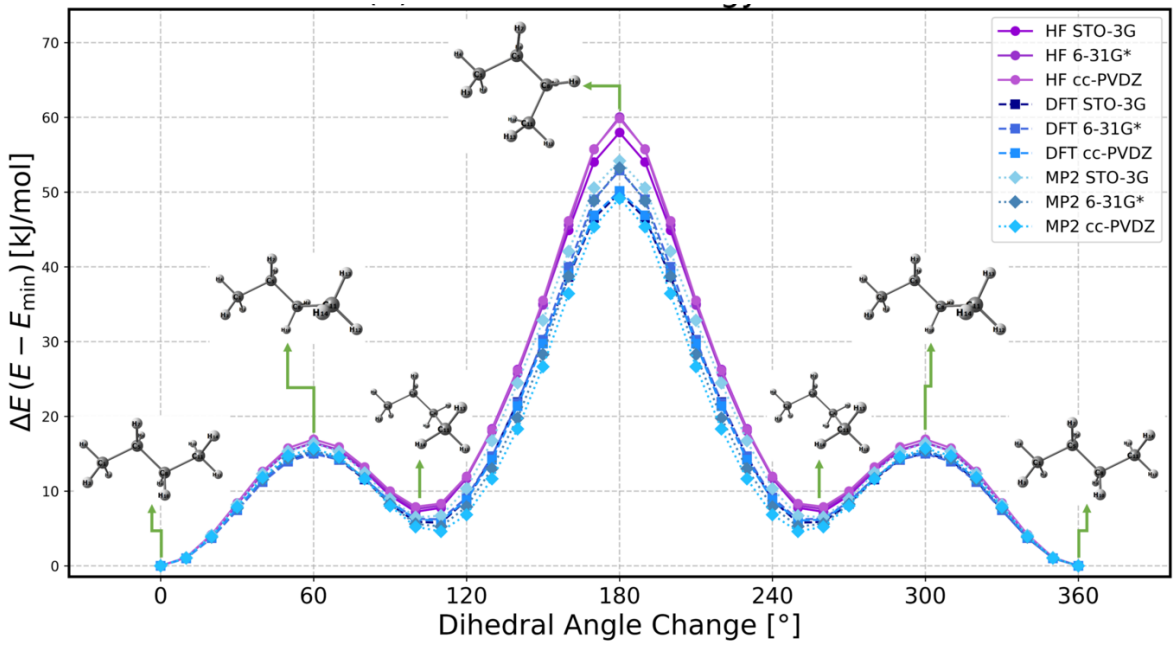

Figure 1: Relative energy profile of the n-butane molecule at various levels of theory and basis set obtained by varying the dihedral angle.

Introduction

The Potential Energy Surface (PES) scan is a computational technique widely used in computational chemistry to analyze the energy landscape of a molecule as a function of its various degrees of freedom, that is, its internal geometrical structure, particularly features such as bond distance, bond angles, and dihedral angles. The PES of a molecule is especially useful for understanding the stability of different molecular conformations, providing insights into both stable and unstable conformers. This enables the identification of relative energy differences among these conformers, helping to predict the most stable molecular configuration [1]; [2]. Additionally, PES aids in analyzing rotational and torsional barriers that must be overcome for molecular rotation about its bonds, which significantly impacts molecular dynamics and compound reactivity[3]. Moreover, PES facilitates the understanding of reaction pathways by identifying transition states and intermediates, allowing for the calculation of the activation energy required for a particular reaction to occur[3]; [4]. PES data can also provide spectroscopic insights, such as predicting vibrational modes and frequencies, which are directly influenced by changes in molecular geometry[5]. There is a plethora of computational chemistry packages available to perform electronic structure calculations. However, in many of these packages, the information on performing a dihedral scan is not readily available. In this work, we attempt to build a pedagogical approach towards performing a dihedral scan using some of the popular electronic structure packages.

Early works in the 1900s aimed at performing PES scans using computational chemistry software tools such as PCMODEL 4.0[6]; [7] and SURFER[7]. Later, different research groups worldwide developed various proprietary tools, the most prominent of which are Gaussian[8] and Q-Chem[9]. In recent years, a plethora of open-source/freeware frameworks have gained traction in research due to their diverse computational capabilities and strong open-source communities. Some notable examples include CP2K[10], GAMESS[11], NWChem[12], ORCA[13], Psi4[14], and PySCF[15], which are the focus of the current

study. In the subsequent paragraphs, we briefly introduce the software programs chosen for the work, followed by the molecular system under investigation.

CP2K is an open-source computational chemistry software package initially released in 2000 and written in the Fortran 2008 programming language. It is well-suited for large-scale molecular simulations, Density Functional Theory (DFT), Molecular Dynamics (MD), and hybrid quantum-classical methods[10].

The General Atomic and Molecular Electronic Structure System (GAMESS) was initially developed in the late 1970s and was primarily written in Fortran. Maintained by the Gordon Research Group at Iowa State University, it provides a comprehensive suite of quantum chemical methods, including Hartree-Fock (HF), post-HF, and coupled-cluster (CC) approaches, making it useful for molecular structure optimization and reaction mechanism studies[11].

Northwest Chemistry (NWChem), initially released in 1994, was developed by a team of researchers and is maintained by the Environmental Molecular Sciences Laboratory (EMSL) at the (PNNL). Its codebase is written in Fortran and designed for high-performance computing (HPC) environments. This supports extensive electronic structure and molecular dynamics simulations, enabling the study of large biomolecules and materials[12].

ORCA was developed in the late 1990s at the Max-Planck-Institut für Kohlenforschung, with contributions from FAccTs GmbH and the broader scientific community. Its codebase is written in C++, and it is widely recognized for its robust implementation of high-accuracy quantum chemistry methods, particularly for transition metal complexes and spectroscopic analysis[13].

Psi4 is a flexible package developed by a global community of researchers[14]. It features a C++/Python-based codebase optimized for electronic structure calculations, emphasizing efficient implementations of wavefunction-based methods such as HF, Møller–Plesset perturbation theory (MP), and CC, making it useful for benchmarking and method development[14].

Python-based Simulations of Chemistry Framework (PySCF) is a Python-based framework whose development began in 2014[15]. It is maintained by a board of directors spanning various academic institutions, along with contributions from a wide range of community developers from both academia and industry. It is designed for seamless integration with automation, supporting DFT and correlated wavefunction methods, while offering ease of customization for advanced quantum chemistry calculations[15]. The summary of the software used for this study can be found in Table 1.

Software	Developer(s)	Year	License
CP2K	CP2K developer group	2000	GNU General Public License
GAMESS	Iowa State University – Quantum Chemistry Group	1977	Proprietary freeware
NWChem	Pacific Northwest National Laboratory	1994	Educational Community License 2.0
ORCA	Frank Neese (Max-Planck-Institut für Kohlenforschung), FACCTs GmbH	1997	Academic, Commercial
Psi4	Initial: Henry F. Schaefer, III (University of Georgia) Currently: world-wide community of developers	2016	GNU General Public License
PySCF	Initial: Qiming Sun, et.al., Currently: world-wide community of developers	2014	Apache-2.0 License

Table 1: Summary of various Computational Chemistry Software used during this study.

Molecular System Chosen for Investigation

For the purpose of performing a PES scan, we work with the n-butane molecule in this study. It is a straight-chain saturated hydrocarbon with the molecular formula C4H10[16]; [17]. Its structure can be represented as CH3-CH2-CH2-CH3[18], and it has a molecular weight of approximately 58.12 g/mol[17]. The n-butane molecule has a structural isomer, isobutane (2-methylpropane), which features a branched configuration with the same molecular formula. In n-butane, all bonds are sigma (σ) bonds. The Carbon-Carbon (C-C) bonds result from the overlap of sp^3 hybrid orbitals of carbon atoms, while the

Carbon-Hydrogen (C-H) bonds form due to the overlap of sp^3 hybrid orbitals of carbon atoms with the 1s orbitals of hydrogen atoms. The C-C bond length in n-butane is ˜1.54 Å, while the C-H bond length is ˜1.09 Å[16]; [19]. The carbon atoms in n-butane adopt a tetrahedral geometry, with H-C-H and C-C-H bond angles close to 109.5°. This arrangement minimizes electron pair repulsion, following the Valence Shell Electron Pair Repulsion (VSEPR) theory[20]; [21].

We chose n-butane for this study due to its significant conformational flexibility around the central C5-C8 (std. C2-C3) single bond. It is the simplest alkane that exhibits gauche-trans isomerization, making it ideal for understanding PES scans across various software packages. The PES results obtained from the rotation of the dihedral angle formed between the planes defined by atoms C1-C5-C8 and C5-C8-C11 give rise to different spatial arrangements or conformations[22]; [23]; [24], as shown in Figure [2(a)-2(d)]. It should be noted that any further mention of the dihedral angle in this work refers specifically to the n-butane angle formed by atoms C1-C5-C8 and C5-C8-C11 as shown in Figure [2(a)-2(d)].

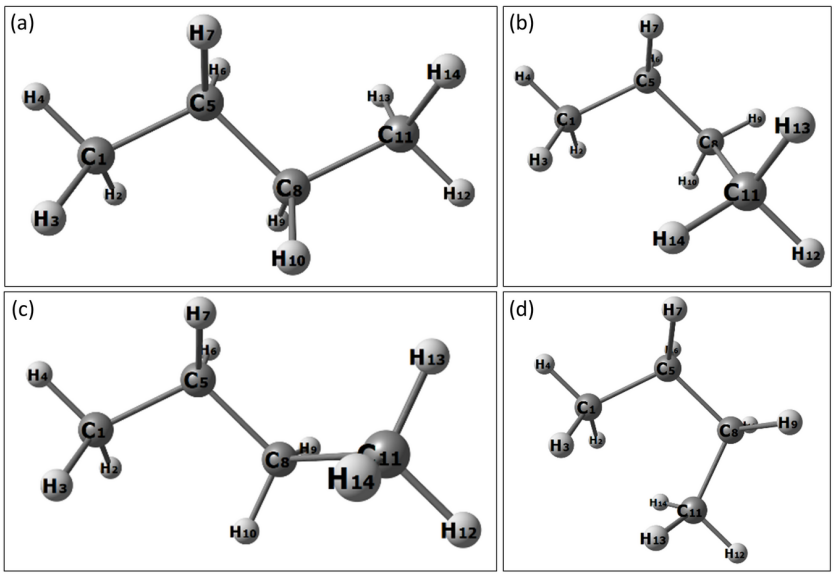

Figure 2: The different conformations of n-butane molecule: (a) Anti-Conformer (antiperiplanar, anti or trans) of n-butane; (b) Gauche-Conformer (synclinal) of n-butane; (c) Eclipsed-Conformer (anticlinal) of n-butane; (d) Cis-Conformer (synperiplanar)

The major conformers of the n-butane molecule include the anti-conformer, gauche-conformer, eclipsed-conformer, and cis-conformer[24]; [25]; [26]. The anti-conformer (also known as the antiperiplanar or trans-conformer) is the most stable conformation with the lowest energy. It occurs when the dihedral angle is ˜180°, where the two terminal methyl groups (CH3) are positioned as far apart as possible, as shown in Figure 2(a). This arrangement minimizes steric hindrance, contributing to the conformer's stability. In contrast, the gauche-conformer (or synclinal-conformer) occurs at ˜80° and ˜280°, where the methyl groups are relatively closer, as shown in Figure 2(b). This proximity introduces steric interactions and torsional strain, leading to a slight increase in energy. The eclipsed-conformer (anticlinal-conformer) forms at ˜120° and ˜240°, aligning the C-H bonds on adjacent carbon atoms as shown in Figure 2(c). This alignment results in torsional strain due to electron cloud repulsions, making this conformation energetically unfavourable. The least stable conformer is the cis-conformer (also known as the synperiplanar-conformer), which occurs when the dihedral angle is ˜0° or ˜360°. It is the maximum steric hindrance and the highest energy conformation of n-butane.

Finally, the cis conformer (also known as the synperiplanar-conformer), as shown in Figure 2(d), occurs when the dihedral angle is ˜0° or ˜360°; here, the two-terminal methyl (CH_3) groups are oriented towards each other within the same plane. This positioning of the methyl groups leads to maximum steric hindrance and gives rise to the highest energy and the least stable conformation of the n-butane molecule.

To further explore the PES scan of n-butane, we outline the methodology and computational details across various software in Section 2, followed by a comprehensive discussion of the results obtained for the PES scan in Section 3. Finally, in Section 4, we present our conclusions and highlight further potential directions for this work.

Methodology & Computation

The process of performing a PES scan generally involves systematically varying the internal coordinates of a molecule, including bond lengths, bond angles, or dihedral angles, and calculating the molecular energy at each step[27]; [28]; [29]. Computationally, two types of PES scans can be performed: the Rigid Scan[30], where only the internal coordinate is varied while all other atomic positions remain fixed, and the Flexible/Relaxed Scan[30], where the molecule's geometry is optimized at each step along with the change in the internal coordinate, allowing other coordinates to adjust to minimize the energy. Due to the additional computational overhead of geometry optimization, flexible scans are more computationally expensive than rigid scans.

In this work, we use the Rigid PES scan, ensuring a consistent workflow across various software tools. This approach minimizes the differences arising from varying geometry optimization techniques implemented in different software. Figure 3 illustrates the general workflow of a rigid PES scan, which involves defining the molecule and its internal coordinates, setting the level of theory, performing incremental calculations, and plotting the obtained energy values against the changing internal coordinates to analyze the PES scan.

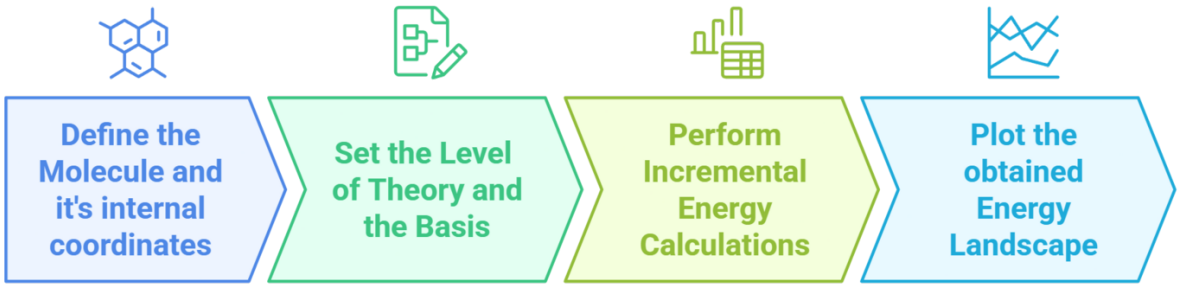

Figure 3: General computational workflow of a PES scan

In this work, we use HF theory[30]; [31], DFT[32]; [33] with Becke's three-parameter exchange functional and the Lee-Yang-Parr correlation functional (B3LYP)[34]; [35]; [36], and Møller–Plesset second-order perturbation (MP2) theory[37]. HF theory is an *ab initio* quantum chemistry method that approximates the many-electron wavefunction using a single Slater determinant[31]; [38]. In this theory, electron-electron interactions are modelled using a mean-field approximation, where each electron moves in the average field of all other electrons[39]. The primary advantage of working with the HF level of theory is its computational efficiency. However, this method lacks an explicit description of electron correlation, which may lead to a systematic overestimation of calculated energy values[39]. Next, we employ DFT, a widely used methodology for calculating the ground-state electron density directly. In this work, we use the B3LYP exchange-correlation functional, which combines B3[35] with LYP[34]. Compared to HF, DFT balances computational cost with accuracy in computational quantum chemistry calculations, accounting for electronic correlation partially through its functional[39]. Finally, we use MP2, a post-HF method that includes electron correlation by treating the HF wavefunction as a zeroth-order approximation and applying second-order perturbation theory[37]. Though MP2 provides more accurate energy estimates by incorporating electronic correlation, it is computationally more expensive than HF and DFT(B3LYP)[39].

Next, the chosen levels of theory must be complemented with an appropriate basis set. In computational quantum chemistry, basis sets are mathematical functions used to approximate the atomic orbitals of

electrons in a molecule[40]. These sets serve as the building blocks for constructing molecular wavefunctions and solving the Schrödinger equation computationally[41]. The basis sets used in this work include the minimal basis set Slater Type Orbital-3 Gaussian (STO-3G)[42] with the HF level of theory, the split-valence 6-31G* basis set[43] with the DFT(B3LYP) level of theory, and the correlation-consistent, zeta-type cc-pVDZ basis set[44] with the MP2 level of theory. In the STO-3G basis set, each atomic orbital is represented as a combination of three Gaussian functions[42]. While computationally efficient, it lacks the flexibility to describe polarization or diffuse functions, leading to relatively lower accuracy in energy calculations[45]. The 6-31G* split-valence basis set, on the other hand, includes polarization functions on atomic orbitals[46], leading to improved accuracy in energy calculations at the cost of increased computational complexity and execution time[45]. Finally, we use Dunning's correlation-consistent cc-pVDZ basis set, which is specifically designed for post-HF calculations[44]. It is optimized for capturing electronic correlation in molecular systems, providing high accuracy in energy computations, though it comes with the highest computational cost among the three basis sets[45].

The objective of employing three levels of theory (HF, DFT, and MP2) along with three different basis sets (STO-3G, 6-31G*, and cc-pVDZ) is to develop a comprehensive understanding of how open-source software can be used to perform computational quantum chemistry calculations. A summary of the chosen levels of theory and basis sets is provided in Table 2.

Level of Theory	Basis Set	Advantage
HF	STO-3G	Offers a fast, computationally efficient method for obtaining an initial energy estimate for the molecular system under study. Although it lacks electron correlation, its minimal basis set makes it ideal for preliminary studies and large systems where speed is crucial.
DFT	6-31G*	Utilizes an exchange-correlation functional to incorporate electron correlation effects, providing a balance between computational efficiency and accuracy. This makes it well-suited for systems of moderate to large size where higher-level methods may be prohibitive.
MP2	cc-pVDZ	Enhances the Hartree–Fock approach by applying a second-order perturbative correction, thus capturing electron correlation in a more rigorous manner. When paired with a correlation-consistent basis set like cc-pVDZ, it achieves improved accuracy for single-point energy calculations.

Table 2: Summary of the Levels of Theory and Basis Sets chosen for the study.

For this study, we primarily use two standard representations of molecular geometry and internal coordinates: the Cartesian coordinate representation[47]; [48] and the Z-matrix representation[47]; [49]. The Cartesian coordinate system specifies the exact location of each atom in three-dimensional space relative to a defined origin. In contrast, the Z-matrix representation defines the positions of atoms relative to previously defined atoms in the molecule, using internal coordinates such as bond lengths, bond angles, and dihedral angles. The Cartesian coordinates and Z-Matrix representations of the n-butane molecule can be found in Tables 3 and 4, respectively.

The Cartesian coordinate representation of a molecule's geometry is relatively straightforward and is readily available in most standard databases. Representing large molecules is easier in this format since each atom's position is independent of the others. In contrast, the Z-matrix representation defines the positions of atoms relative to one another, providing essential internal coordinate information such as bond lengths and bond angles. Additionally, the Z-matrix representation makes it relatively easier to manipulate specific internal coordinates as needed. Following this, we proceed with single-point energy calculations for the n-butane molecule across various software packages to obtain the PES landscape, the details of which are elaborated in the following section.

Atom	X	Y	Z
C	1.37	1.06	3.45
H	0.99	0.22	4.01
H	2.41	0.9	3.24
H	1.25	1.95	4.03
C	0.6	1.19	2.13
H	-0.44	1.34	2.34
H	0.97	2.02	1.58
C	0.77	-0.1	1.3
H	1.81	-0.25	1.09
H	0.39	-0.93	1.85
C	-0.0	0.03	-0.02
H	0.12	-0.86	-0.6
H	-1.04	0.18	0.18
H	0.38	0.87	-0.58

Table 3: Cartesian coordinates representation of the n-butane molecule.

Atom	Reference 1	Bond Length	Reference 2	Bond Angle	Reference 3	Dihedral Angle
C						
H	1	1.07				
H	1	1.07	2	109.47		
H	1	1.07	2	109.47	3	240
C	1	1.54	2	109.47	3	120
H	5	1.07	1	109.47	2	60
H	5	1.07	1	109.47	2	180
C	5	1.54	1	109.47	2	300
H	8	1.07	5	109.47	1	300
H	8	1.07	5	109.47	1	60
C	8	1.54	5	109.47	1	180
H	11	1.07	8	109.47	5	180
H	11	1.07	8	109.47	5	300
H	11	1.07	8	109.47	5	60

Table 4: Z-matrix representation of the n-butane molecule.

Software (Molecular Construction and PES Scan Implementation with Different Quantum Chemistry Software)

In our case, we first construct the n-butane molecule in Avogadro[50] and obtain its Cartesian coordinates at a 0° dihedral angle. The open-source computational chemistry software used in this work may be broadly classified into Command-Line Interface (CLI) software and Python-Integrated (PI) software based on their interaction modes with the user. In this study, CP2K, GAMESS, ORCA, and NWChem were utilized in CLI mode, requiring users to execute calculations via terminal commands, making them well-suited for direct HPC batch processing. On the other hand, Psi4 and PySCF are designed for seamless Python integration, allowing calculations to be performed within Python scripts, thereby providing greater flexibility for workflow automation.

As a CLI-based tool, CP2K takes input in the form of an *.inp* file and accepts molecular structure information as Cartesian coordinates or a Z-matrix representation. The Cartesian coordinates at each dihedral angle are then calculated using the Atomic Simulation Environment (ASE). CP2K's default implementations of HF, DFT, and MP2, such as Gaussian Plane Wave (GPW) or Quickstep, do not support all-electron calculations. To enable all-electron calculations in CP2K, we use the Gaussian and Augmented Plane Wave (GAPW) method. Since a CP2K input file allows only a single operation at a

time, automating the sequential execution of multiple input files is necessary. This automation is achieved using shell/bash scripting, which also facilitates the collection of final results from each output file.

The computational steps to perform a PES scan using CP2K are as follows:

1. Obtain butane Cartesian coordinates as a *.xyz* file from Avogadro.
2. Use a Python script with ASE to calculate the coordinates at each dihedral angle from 0° to 360° in 36 steps.
3. Generate the *.inp* input file for CP2K, selecting the computational method and basis set.
4. Use a shell script to sequentially execute CP2K input files for each dihedral angle.
5. Extract energy results from the .out output files and generate the PES curve using Python plotting libraries such as matplotlib or Plotly.

For detailed scripts related to CP2K input files, Python automation, and shell scripting, refer to [51].

GAMESS is a command-line interface (CLI)-based computational chemistry software that can be run in an external executable mode. It requires an input file in *.inp* format, which specifies details such as the computational method, basis set, molecular geometry, and atomic coordinates. This input file can either be manually written or generated using external software packages like Avogadro or wxMacMolPlt. To perform the PES scan using GAMESS, we begin by creating an input file for a specific dihedral angle, for example, 0°. This file contains all essential information, including atomic coordinates, the chosen basis set, and the computational method. We then calculate the coordinates for each subsequent dihedral angle in increments up to 360°. Each input file is executed via the command line, producing an output file (*.out*) containing energy results.

To streamline the process, we have automated the workflow using Python. The automation script performs the following tasks:

1. Generates GAMESS input files for each dihedral angle.
2. Executes each input file sequentially via the command line.
3. Extracts energy values from the corresponding .out files.
4. Compiles the extracted data into a structured format containing energy values and computational parameters.

The final set of energy values is used to generate the PES scan graph using Python plotting libraries such as matplotlib or Plotly. We have used the GAMESS Windows version for our computation. For details on the Python automation script and GAM ESS input file format, refer to [51].

ORCA is a proprietary, general-purpose quantum chemistry package that is freely available for academic researchers. It features a CLI-based interface that takes input in the form of an *.inp* file and accepts molecular structure information in both Cartesian coordinates and Z-matrix formats.

Additional constraints must be applied to the molecule to perform a Rigid PES scan using Cartesian coordinates. Similar to the previously mentioned tools, the n-butane structure is obtained from Avogadro in Z-matrix format. However, it is important to note that ORCA uses a non-standard Z-matrix format, which requires slight modifications to the input file. This format typically includes all reference atom numbers preceding the standard bond length, angle, and dihedral angle values found in a conventional Z-matrix format. The computational steps to perform a rigid PES scan using ORCA are as follows:

1. Use Avogadro to create an ORCA input file template for butane, selecting the computational method and basis set.
2. Adjust the Z-matrix format in the input file to match ORCA's requirements.
3. Modify and add the *%paras* block, in combination with internal coordinates, to vary the dihedral angle from 0° to 360° in 36 steps.
4. Extract energy results from the *.out* output file and generate the PES curve using Python plotting libraries such as matplotlib or Plotly.

For further details on the ORCA input file, refer to [51]. Additionally, ORCA can be paired with the Atomic Simulation Environment (ASE) for seamless integration with other software packages and workflow automation.

NWChem is an open-source, high-performance computational chemistry software designed to run on Unix-like operating systems. It provides a command-line interface (CLI) and supports a variety of quantum mechanics (QM), molecular mechanics (MM), and MD calculations. Since Windows is not natively supported, we utilize the WSL2 environment to execute NWChem.

NWChem requires an input file in *.nw* format, which defines the computational method, basis set, and molecular structure. This file can be manually written using the reference manual or generated using external software like Avogadro. Subsequently, we calculate the coordinates for each dihedral angle step and generate a corresponding input file for each angle.

To automate the PES scan workflow, we employ a combination of Python scripting and shell scripting. The automation process consists of the following steps:

1. Generate the initial NWChem input file for n-butane using Avogadro.
2. Use a Python script to compute the Cartesian coordinates for each dihedral angle from 0° to 360° in 36 steps.
3. Create separate *.nw* input files for each angle, specifying the computational parameters.
4. Use a shell script to sequentially execute each input file via the command line.
5. Extract energy results from the *.out* files and compile them into a structured format.
6. 6. Plot the PES curve using Python libraries such as matplotlib or Plotly.

This workflow ensures full automation, from input file generation to final PES visualization. For further details on the NWChem input file format, Python automation script, and shell scripting, refer to [51].

The Python-integrated software Psi4 and PySCF both support the use of Cartesian coordinates and Z-matrix molecular representations to perform Rigid PES scans. Psi4 can be used both as an executable in CLI mode or in API mode via Python scripting; in this work, we use the latter. PySCF, on the other hand, is specifically designed as a Python-based package.

We initially generate the molecule's Cartesian coordinates using open-source molecular building software such as Avogadro, where we construct the n-butane molecule and perform geometry optimization. We then retrieve the Cartesian coordinates of the optimized n-butane molecule via an *.xyz* file and convert them to the Z-matrix format, which simplifies performing the PES scan.

The computational steps for performing PES using the Psi4 API and PySCF are as follows:

1. Define the molecular geometry in Z-matrix format within the Psi4/PySCF Python files using the *psi4.geometry( )* and *pyscf.gto.M( )* methods, respectively.
2. Set up a loop in Python to vary the dihedral angle, incrementing it at each step and performing single-point energy calculations using *the psi4.energy( )* function from the Psi4 library and the *scf.RHF( )* function from the PySCF library to obtain the molecular energy at each conformation.
3. Store and analyze the energy results to generate the PES curve using Python plotting modules such as *matplotlib* or *plotly*.

Further details about both packages, along with their implementation code in Python, are available in [51] for Psi4 and PySCF.

As an alternative to the above-provided method, is to perform the dihedral rotation by directly manipulating the Cartesian coordinates of the molecules using external methods. In this case, we may use *SciPy's* rotation module to perform the rotation about the dihedral axis. Similar to the previous example, the following steps may be performed:

1. The butane molecule is defined using Cartesian coordinates and stored in a string format. The coordinates are retrieved as a *NumPy* array.
2. The displacement vector of one of the central dihedral atoms from the origin, and the dihedral axis are required, while the former is given as an input to the class *scipy.spatial.transform.Rotation*. The coordinates of the atoms to be rotated are picked, the displacement is subtracted, and the rotation is performed. After rotation, the coordinates are restored to the same distance from the origin by adding back the displacement vector, but with rotation about the dihedral axis.

3. As mentioned previously, the transformed coordinates are input into the class *gto.M( ),* and the class for the relevant level of theory is selected, and the energy is obtained.

Recent developments in these software packages include Python-integrated workflows for traditionally CLI-based software such as GAMESS via pyGAMESS[52], and CP2K via pyCP2K[53], which are beyond the scope of this work.

Results & Discussion

Performing a PES scan using six computational chemistry software packages across three levels of theory and basis sets resulted in 18 distinct PES curves for n-butane, as shown in Figure 4. Each row in the figure corresponds to a specific software package—CP2K, GAMESS, NWChem, ORCA, Psi4, and PySCF—while each column represents a particular level of theory and basis set, where the first column corresponds to results obtained for HF with the STO-3G basis set, followed by DFT with B3LYP and the split-valence 6-31G* basis set in the second column, and finally the MP2 method with the correlation-consistent double-zeta cc-pVDZ basis set in the final column.

The PES results reveal a consistent waveform of the PES scan across all software and levels of theory. Where the highest-energy cis-conformer of n-butane is observed at 0° and 360°, while the eclipsed conformers appear at 120° and 240°. The gauche conformers, corresponding to local minima, are found at 80° and 280°, and the most stable, lowest-energy anti-conformer occurs at 180°. The consistency in this waveform pattern confirms the reliability of the results obtained and may be attributed to using the same initial conformation of n-butane, followed by following a consistent computation workflow across all software.

We also compare the exact energy values obtained across the six software packages for the different levels of theory and basis sets, as shown in Figure 5. As shown in Figure 5(a) for HF with the STO-3G basis set, the energy values exhibit strong agreement across all software, demonstrating the robustness of these calculations at this level of theory.

However, as seen in figure 5(b) for DFT with the 6-31G* basis set, two distinct energy sets emerge: the first, with slightly higher PES energy values at ˜ -158.32 Ha, is observed for CP2K, ORCA, and GAMESS, while the second, with relatively lower energy values at ˜ -158.44 Ha, is obtained using PySCF, Psi4, and NWChem. A similar trend is observed for MP2 with the cc-pVDZ basis set as shown in figure 5(c), where GAMESS produces a higher energy set at ˜ -157.3 Ha, while the remaining software packages—NWChem, CP2K, ORCA, Psi4, and PySCF—yield slightly lower energy values at ˜ -158.0 Ha.

These differences in resulting energy values may be attributed to the subtle changes in PES energy predictions across software implementations and computational methodologies. The observed discrepancies may also highlight the differences in numerical integration techniques, default convergence criteria, and basis set implementations in each software package, which would benefit from further study. Nevertheless, the qualitative agreement in waveforms and conformer energy rankings indicates the reliability of these methods for PES calculations.

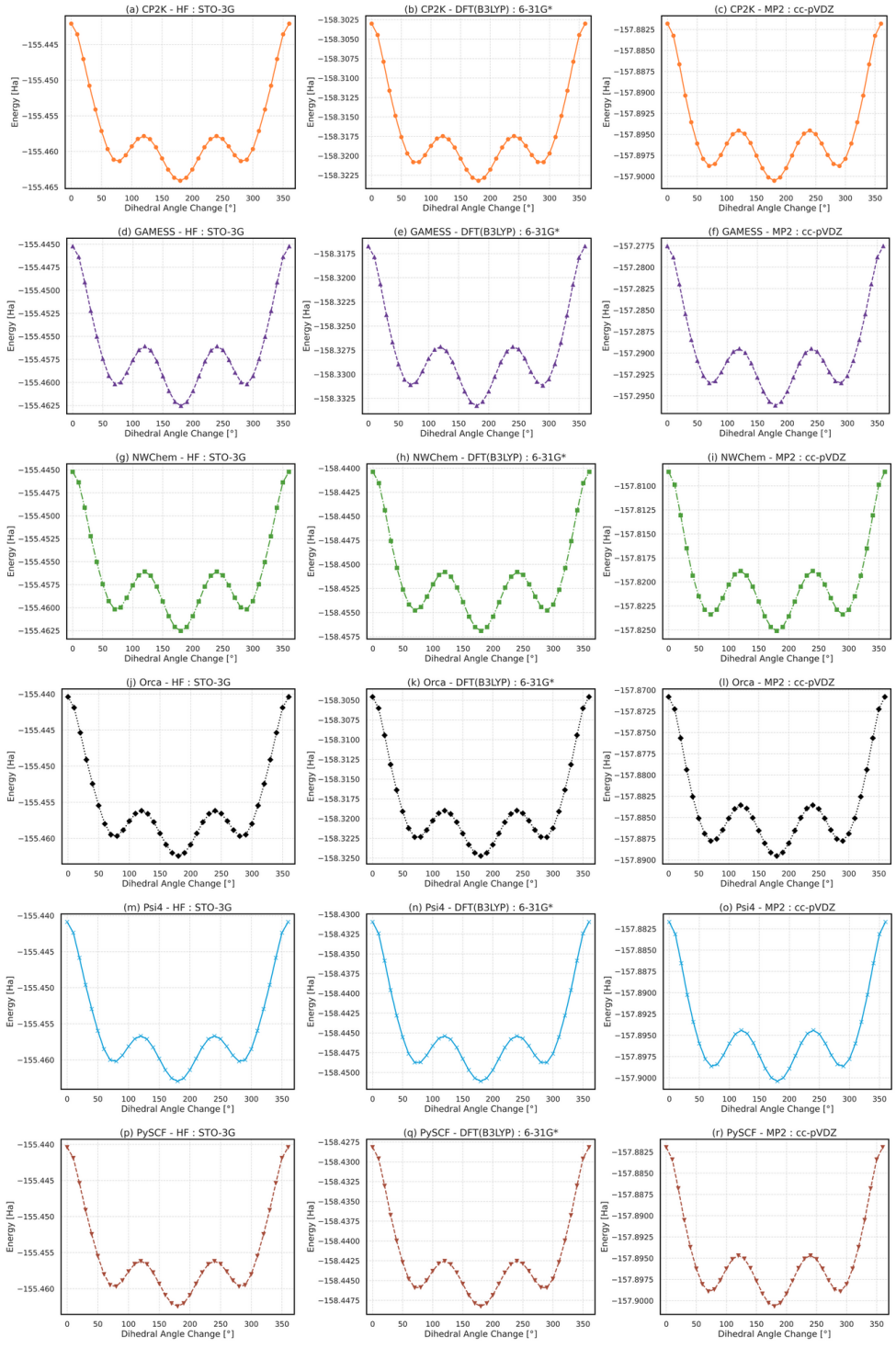

Figure 4: Results obtained by performing PES scan for n-butane molecule across various open-source software using various levels of theory and basis sets, each row corresponds to results from a particular software and each column represents particular level of theory and associated basis set used, where: (a) CP2K – HF : STO-3G, (b) CP2K – DFT(B3LYP) : 6-31G*, (c) CP2K – MP2 : cc-pVDZ, (d) GAMESS – HF : STO-3G, (e) GAMESS – DFT(B3LYP) : 6-31G*, (f) GAMESS – MP2 : cc-pVDZ, (g) NWChem – HF : STO-3G, (h) NWChem – DFT(B3LYP) : 6-31G*, (i) NWChem – MP2 : cc-pVDZ, (j) Orca – HF : STO-3G, (k) Orca – DFT(B3LYP) : 6-31G*, (l) Orca – MP2 : cc-pVDZ, (m) Psi4 – HF : STO-3G, (n) Psi4 – DFT(B3LYP) : 6-31G*, (o) Psi4 – MP2 : cc-pVDZ, (p) PySCF – HF : STO-3G, (q) PySCF – DFT(B3LYP) : 6-31G*, (r) PySCF – MP2 : cc-pVDZ.

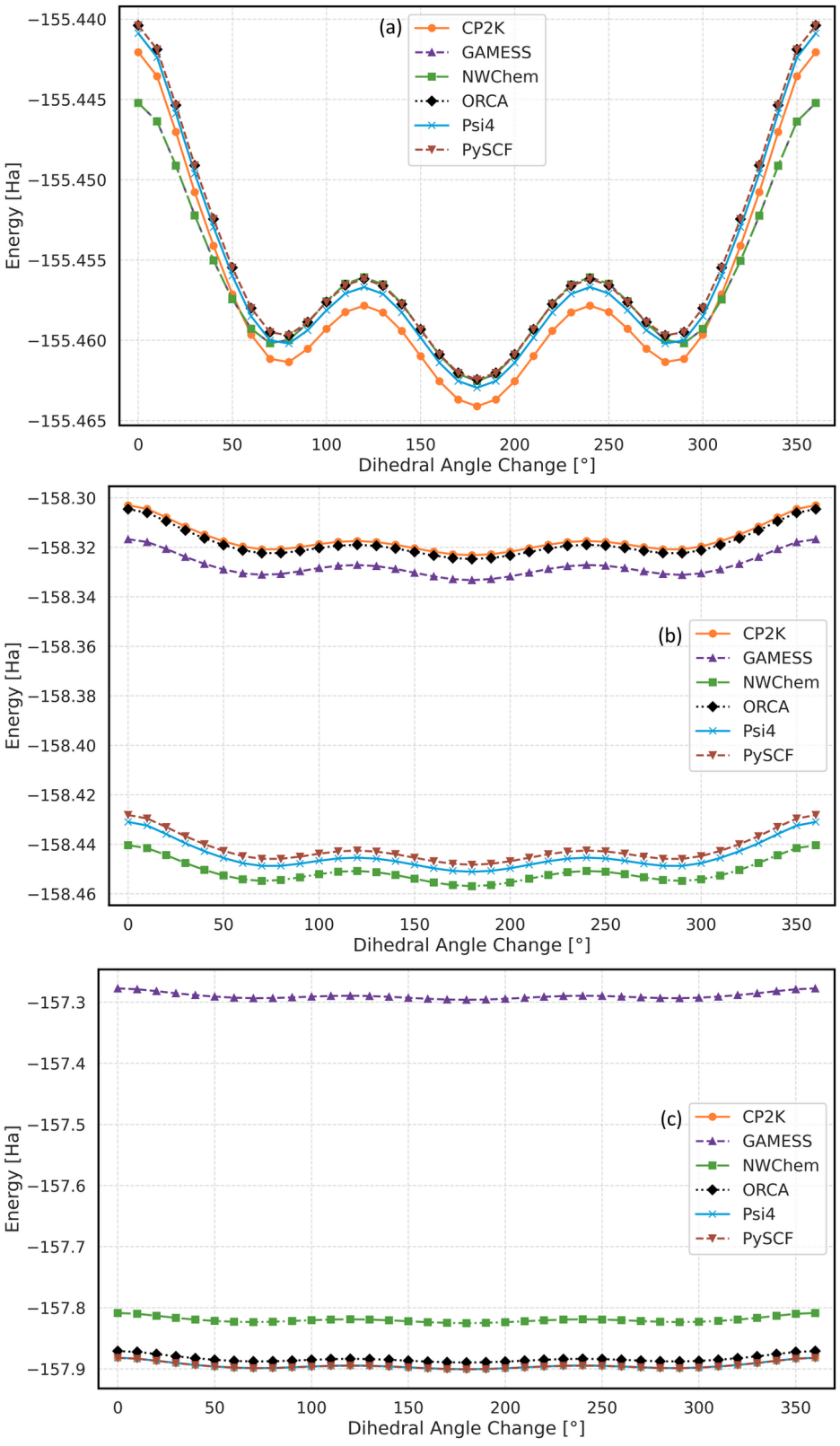

Figure 5: Results of the n-butane PES scan on various open-source software platforms (CP2K, GAMESS, NWChem, Orca, Psi4, PySCF) categorized based on the level of theory and basis sets used, where: (a) HF using STO-3G basis set, (b) DFT with B3LYP functional using 6-31G* basis set, (c) MP2 using cc-pVDZ basis set.

The exact energy values obtained for the conformers of n-butane (cis, eclipsed, gauche, and anti) across the PES scan are summarized in Table 5 for HF using STO-3G, Table 6 for DFT(B3LYP) using 6-31G*, and Table 7 for MP2 using cc-pVDZ. These tables provide a quantitative comparison of the computed PES landscapes, offering insights into software-specific variations obtained for the energy values of the various conformers while reaffirming the consistency of fundamental conformational trends. All in all, these results underscore the significance of software choice in high-accuracy quantum chemistry simulations, particularly the need to work with a single software across all experiments performed to obtain computational quantum chemistry results to be considered reliable, especially when relative energies are calculated for different molecules benchmarked against experimental values.

n-butane Conformer	Angle [°]	CP2K	GAMESS	NWChem	ORCA	Psi4	PySCF
Cis	0	-155.44	-155.45	-155.45	-155.44	-155.44	-155.44
Gauche	80	-155.46	-155.46	-155.46	-155.46	-155.46	-155.46
Eclipsed	120	-155.46	-155.46	-155.46	-155.46	-155.46	-155.46
Anti	180	-155.46	-155.46	-155.46	-155.46	-155.46	-155.46
Eclipsed	240	-155.46	-155.46	-155.46	-155.46	-155.46	-155.46
Gauche	280	-155.46	-155.46	-155.46	-155.46	-155.46	-155.46
Cis	360	-155.44	-155.45	-155.45	-155.44	-155.44	-155.44

Table 5: n-butane conformer absolute energies in Hartree (Ha) using various open-source software using HF with STO-3G basis set.

n-butane Conformer	Angle [°]	CP2K	GAMESS	NWChem	ORCA	Psi4	PySCF
Cis	0	-158.3	-158.32	-158.44	-158.3	-158.43	-158.43
Gauche	80	-158.32	-158.33	-158.45	-158.32	-158.45	-158.45
Eclipsed	120	-158.32	-158.33	-158.45	-158.32	-158.45	-158.44
Anti	180	-158.32	-158.33	-158.46	-158.32	-158.45	-158.45
Eclipsed	240	-158.32	-158.33	-158.45	-158.32	-158.45	-158.44
Gauche	280	-158.32	-158.33	-158.45	-158.32	-158.45	-158.45
Cis	360	-158.3	-158.32	-158.44	-158.3	-158.43	-158.43

Table 6: n-butane conformer absolute energies in Hartree (Ha) using various open-source software using DFT and B3LYP functional with 6-31G* basis set.

n-butane Conformer	Angle [°]	CP2K	GAMESS	NWChem	ORCA	Psi4	PySCF
Cis	0	-157.88	-157.28	-157.81	-157.87	-157.88	-157.88
Gauche	80	-157.9	-157.29	-157.82	-157.89	-157.9	-157.9
Eclipsed	120	-157.89	-157.29	-157.82	-157.88	-157.89	-157.89
Anti	180	-157.9	-157.3	-157.83	-157.89	-157.9	-157.9
Eclipsed	240	-157.89	-157.29	-157.82	-157.88	-157.89	-157.89
Gauche	280	-157.9	-157.29	-157.82	-157.89	-157.9	-157.9
Cis	360	-157.88	-157.28	-157.81	-157.87	-157.88	-157.88

Table 7: n-butane conformer absolute energies in Hartree (Ha) using various open-source software using MP2 with cc-pVDZ basis set.

Conclusion

This work presents the detailed process, methodologies, and comparative analysis of the PES scan of the n-butane molecule using six different prominent open-source quantum chemistry software packages. We

successfully explore the torsional potential energy changes in n-butane by varying the dihedral angle, specifically the C–C–C–C angle, from 0° to 360° in increments of 10°.

It is evident that the PES scan is a vital tool in computational chemistry as it helps us understand the relationship between molecular geometry and energy, providing insights into the preferred conformations of a molecule and the energy barriers associated with interconversion between these conformations. For n-butane, PES reveals the energy variations as the molecule rotates around its central C–C bond, capturing the equilibrium or minimal energy conformation (anti-conformer) and transition states or maximal energy conformation (cis-conformer) of the molecule.

We have observed that the overall shape of the PES curves across all the software packages showed consistency in the key features, mainly the waveform. We may conclude that the selection of the level of theory and basis set plays a pivotal role in determining the accuracy and computational efficiency of PES calculations. While using HF with STO-3G is a reasonable starting point for qualitative analysis, using DFT(B3LYP) with 6-31G* strikes a balance between precision and cost. MP2, although computationally expensive, offers enhanced accuracy for conformational energy landscapes when paired with advanced basis sets like cc-PVDZ, capturing more correlations. Together, these methods enable a comprehensive exploration of the n-butane PES, illustrating the importance of theoretical and methodological considerations in computational chemistry while performing quantum chemistry simulations.

In computational chemistry, PES plays a crucial role—it represents how a molecule's energy varies with changes in its geometric arrangement or atomic coordinates[53]. By mapping the electronic energy to molecular geometries, PES enables the theoretical exploration of molecular shapes and transformations through the framework of the Schrödinger equation. As such, detailed characterization of PES is indispensable for a wide range of applications. These include the computation of reaction rate coefficients, since chemical reactions proceed along pathways defined on the PES, and an accurate surface is required for reliable kinetic modelling[54]. Additionally, PES forms the backbone of molecular dynamics force fields, where energy changes arising from interatomic interactions must be consistently represented[55]. Accomplishing this relies on access to chemical data related to potential energy surfaces, reaction pathways, and the corresponding chemical species.

Apart from what has been discussed in the paper, PES can be utilized to find the most stable conformation of a drug molecule and then analyze the HOMO and LUMO of that conformation to understand how the molecule interacts with its target. PES is a multidimensional representation that maps the energy of a chemical system based on its internal coordinates. It reveals key features like stationary points—including local minima that correspond to stable structures, and saddle points that indicate transition states—both of which are essential for understanding reaction mechanisms[56].

We conclude by emphasizing the importance of selecting a single software, a consistent methodology, an appropriate level of theory, and a suitable basis set based on the specific goals of the analysis, the desired precision, and the available computational resources to obtain reliable and reproducible quantum chemistry computational results. This work may serve as a primer for beginners willing to explore the field of computational chemistry.

Data Availability

The code and scripts supporting the findings of this study are available at https://github.com/qclairvoyance/n-butane-pes-scans.

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Conflict of Interest

All authors declare that they have no conflicts of interest.

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