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Electrode Geometry-Controlled Quantum Transport in Au–Pentane–Au Molecular Junctions: A DFT–NEGF and Machine Learning Study

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Abstract

Molecular electronics offers a route toward continued device miniaturization, but reliable control of charge transport at the molecular scale requires a detailed understanding of the metal–molecule interface. In particular, the role of electrode geometry in determining transport behaviour remains less systematically explored than molecular structure and contact chemistry. Here, we investigate the influence of atomic-scale electrode geometry on the structural, electronic, quantum-transport, thermoelectric, and noise properties of Au–pentane–Au molecular junctions using a combined density functional theory–non-equilibrium Green's function (DFT–NEGF) and machine learning framework. Six representative electrode configurations—Flat Au(111), Pyramidal, Single Apex, Multi-Atom Tip, Nanowire, and Rough Surface—were structurally optimized and systematically compared while maintaining the same pentane molecular backbone and Au–S contact chemistry.

The calculations reveal pronounced geometry-dependent variations in Au–S bonding, coordination number, contact area, molecular tilt, charge transfer, electronic-state alignment, and molecule–electrode coupling. These structural and electronic changes directly control quantum transport, with the calculated conductance decreasing from 0.92 G_0 for Flat Au(111) to 0.56 G_0 for the Single Apex configuration. Transmission, current–voltage characteristics, charge redistribution, and interface dipole analysis consistently demonstrate that highly coordinated and extended contacts provide stronger electronic coupling and more efficient transmission pathways. Thermoelectric calculations reveal an opposing trend: lower-coordination contacts exhibit enhanced Seebeck coefficients because of stronger energy dependence of transmission near the Fermi level, whereas the Flat Au(111) junction provides the highest calculated power factor and $ZT \approx 0.68$. Shot noise, Fano factor, low-frequency noise, and Hooge-parameter analysis further demonstrate increasing transport fluctuations as electrode coordination decreases.

To accelerate transport prediction, a dataset of 1500 configurations were constructed from structural and electronic descriptors extracted from the DFT–NEGF calculations. Among the tested models, XGBoost achieved the highest predictive performance, with a testing R^2 of 0.988, RMSE of 0.010 G_0 , and MAE of 0.007 G_0 . Feature-importance analysis identified Au–S bond length, HOMO–LUMO gap, coupling strength, DOS at the Fermi level, and Au s PDOS as the dominant predictors. The trained model successfully predicted conductance for previously unseen electrode configurations, demonstrating its potential for rapid screening of molecular junction structures.

Key Words

Molecular electronics; Electrode geometry; Au–pentane–Au molecular junctions; DFT–NEGF; Machine learning

1. Introduction

The continuous miniaturization of electronic devices has driven the remarkable growth of modern microelectronics for more than five decades. Following Moore's law, the increasing number of transistors on a single chip has greatly improved computing performance and energy efficiency. However, as device dimensions have reached the nanometer scale, conventional complementary metal–oxide–semiconductor (CMOS) technology faces fundamental challenges, including quantum tunnelling, leakage currents, heat generation, short-

channel effects, and fabrication complexity [1–4]. These limitations have motivated the search for new technologies that can overcome the scaling limits of silicon-based electronics.

Among the emerging alternatives, molecular electronics has become a promising research area because individual molecules can function as active electronic components at the ultimate limit of miniaturization. The concept, first proposed by Feynman and later developed by Aviram and Ratner through the molecular rectifier, opened the possibility of using single molecules in electronic circuits [5,6]. Advances in experimental techniques, such as mechanically controllable break junctions, scanning tunnelling microscope break junctions, conductive atomic force microscopy, and electromigrated nanogaps, have enabled the reliable fabrication and characterization of single-molecule junctions [7–10]. These developments have significantly improved our understanding of charge transport at the molecular scale.

Unlike conventional semiconductor devices, charge transport through molecular junctions is governed by quantum mechanics because the molecular length is comparable to the electron phase coherence length. The conductance depends strongly on the molecular electronic structure, the alignment of molecular orbitals with the electrode Fermi level, and the strength of metal–molecule coupling. To study these effects, Density Functional Theory (DFT) combined with the Non-Equilibrium Green's Function (NEGF) formalism has become the most widely used first-principles approach for investigating electron transport in molecular junctions [11–15]. The NEGF–DFT method provides detailed information on transmission spectra, density of states, conductance, and current–voltage characteristics, making it an essential tool for understanding transport mechanisms at the atomic scale. A key feature of coherent electron transport is quantum interference, which results from the wave nature of electrons. Electron waves travelling through different molecular pathways may interfere constructively or destructively, leading to enhanced or suppressed conductance. Unlike chemical modification, quantum interference offers a direct quantum-mechanical approach for tuning the electrical properties of molecular junctions [16–20]. This phenomenon has attracted considerable interest for the design of molecular switches, rectifiers, thermoelectric devices, and low-power nano-electronic components. Recent studies have also shown that interference effects are highly sensitive to molecular symmetry, orbital connectivity, and the interaction between the molecule and metallic electrodes [21,22].

Besides the molecular structure, the metal–molecule interface strongly influences electron transport. Parameters such as the anchoring group, adsorption site, atomic coordination, crystallographic orientation, and electrode morphology determine the strength of metal–molecule coupling and affect charge transfer, orbital hybridization, and energy-level alignment [23–26]. Even small changes in the contact geometry can produce large variations in conductance. Although the effects of molecular length, conjugation, anchoring chemistry, and electrode materials have been widely studied, the influence of electrode geometry itself remains comparatively less explored, particularly for saturated molecular systems.

Among saturated hydrocarbons, pentane (C_5H_{12}) provides an ideal model for studying geometry-dependent electron transport. As a linear alkane with a large HOMO–LUMO energy gap, charge transport occurs mainly through off-resonant tunnelling, making its conductance highly sensitive to metal–molecule coupling. Unlike conjugated molecules, pentane allows the effect of electrode geometry to be examined more clearly. In realistic molecular junctions, gold electrodes often contain pyramidal tips, stepped surfaces, and atomic protrusions rather than perfectly flat contacts. These structural variations modify the local electronic environment and the overlap between molecular orbitals and electrode states, thereby influencing electron transmission through the junction [27–30]. Understanding these effects is essential for improving the performance and reliability of molecular electronic devices.

Although the NEGF–DFT method provides reliable predictions of transport properties, it is computationally demanding because every junction geometry requires independent geometry optimization and self-consistent transport calculations. This challenge becomes more significant when many electrode configurations are considered. Recently, artificial intelligence (AI) and machine learning (ML) have emerged as efficient tools for accelerating quantum transport studies. By learning the relationship between structural descriptors and transport

properties from first-principles data, ML models can rapidly predict conductance and transmission characteristics with much lower computational cost. Algorithms such as Random Forests, Support Vector Regression, Artificial Neural Networks, Gradient Boosting, and Graph Neural Networks have shown promising performance in molecular electronics [31–35]. Combining AI with NEGF–DFT therefore offers a practical approach for rapid screening and optimization of molecular junctions.

In this work, we investigate the influence of gold electrode geometry on electron transport through Au–pentane–Au molecular junctions using the NEGF–DFT framework together with machine learning techniques. Different electrode geometries with varying atomic coordination are systematically examined while maintaining the same molecular backbone and contact chemistry to isolate the effect of contact geometry on transport behaviour. Machine learning models are further employed to identify the geometric parameters that most strongly affect conductance and to develop predictive models for transport properties.

2. Model Construction and Electrode Geometry

The performance of a molecular junction depends not only on the electronic structure of the molecule but also on how the molecule is connected to the electrodes. Changes in the atomic arrangement at the metal–molecule interface can alter orbital overlap, charge transfer, energy-level alignment, and ultimately the flow of electrons through the junction [26,28,31]. To understand these effects, six Au–pentane–Au molecular junctions with different electrode geometries were constructed. The molecular backbone, anchoring chemistry, and all computational settings were kept identical so that changes in transport properties could be attributed primarily to the electrode geometry.

The scattering region consists of a sulphur-terminated pentane (C_5H_{12}) molecule placed between two gold electrodes. Sulphur atoms were used as anchoring groups because Au–S bonding provides a well-established contact configuration in single-molecule electronic junctions and has been extensively investigated experimentally and theoretically [7,8,28,31,68]. The Au–S bonding configuration and electrode separation were maintained throughout the study to ensure a consistent comparison among all junction models.

In practical experiments, metallic electrodes produced using mechanically controllable break-junction (MCBJ) and scanning tunnelling microscope break-junction (STM-BJ) techniques do not necessarily form perfectly flat surfaces. Atomic-scale contacts can contain low-coordination atoms, pyramidal structures, atomic-scale tips, and other local variations in electrode morphology [7,8,28,31]. Such structural variations modify the local coordination environment and the molecule–electrode interaction. Accordingly, six representative contact geometries were investigated in the present work. Their structural features are summarized in Table 1, and schematic illustrations are presented in Figure 1.

2.1 Electrode Geometry Models

Six different contact geometries were selected to represent distinct atomic arrangements relevant to molecular junctions. A Flat Au(111) surface (M1) was used as the reference configuration. Its relatively extended contact provides interaction between the sulphur anchoring atom and several neighboring gold atoms, resulting in a comparatively strong molecule–electrode interaction [26,28,31].

The Pyramidal electrode (M2) represents a sharp metallic contact in which the coordination of atoms decreases toward the apex. Such changes in contact geometry can substantially influence molecular conductance and the calculated electronic structure of the junction [26,28,30].

In the Single-Apex atom model (M3), the molecule is connected through a highly localized gold contact on each side. Reduced coordination at the contact can weaken molecule–electrode coupling and modify the transmission characteristics of the junction [26,28,31]. Because quantum transport depends sensitively on the available transmission pathways, localized contacts can also modify quantum-interference effects [18,20–25].

The Multi-Atom Tip configuration (M4) replaces the single apex contact with a small group of gold atoms. The presence of several contact atoms provides additional electronic pathways between the molecule and electrodes.

Depending on the electronic structure and phase relationship of these pathways, constructive or destructive quantum interference can occur [18,20–25].

The Nanowire contact (M5) introduces a narrow metallic bridge between the bulk electrode and the molecular contact. Atomic-scale metallic wires can exhibit strongly quantized conductance and pronounced dependence on their atomic configuration [12,13,31,58]. Consequently, the nanowire geometry provides a useful model for examining the influence of reduced-dimensional electrode contacts on molecular transport.

Finally, a Rough Surface model (M6) was constructed to represent an irregular electrode containing atomic protrusions, steps, and local structural disorder. Such variations can modify the local coordination and molecule–electrode coupling and can introduce additional scattering pathways [26,27,30]. The initial structural parameters used for constructing all six models are listed in Table 1.

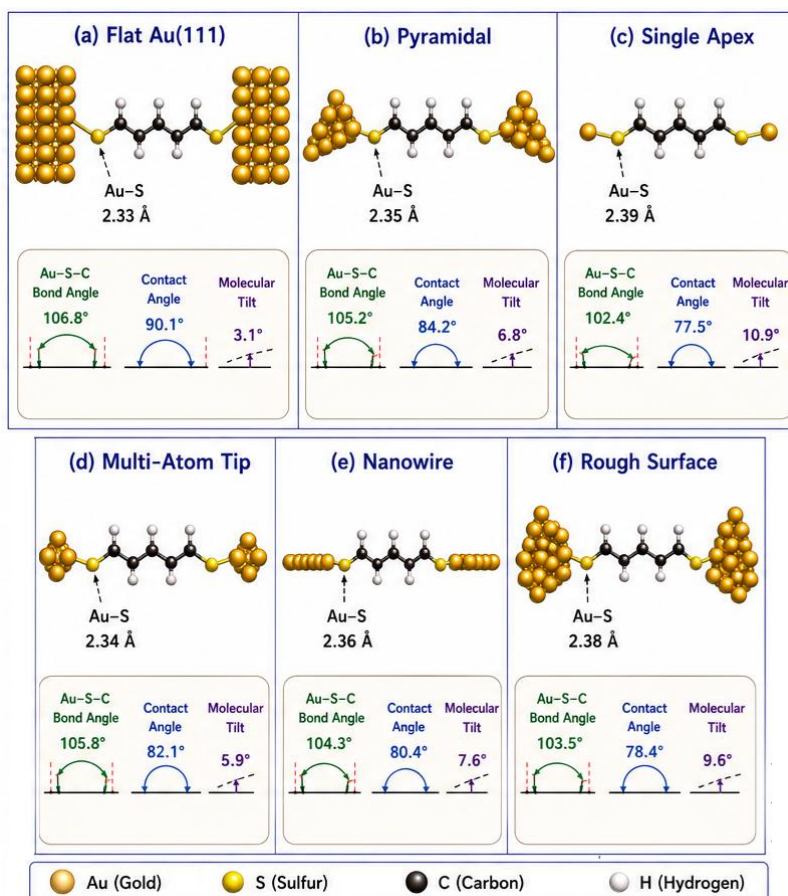


Figure 1. Schematic representation of the six Au–pentane–Au molecular junctions: (a) flat electrode, (b) pyramidal electrode, (c) single-apex atom, (d) multi-atom tip, (e) nanowire contact, and (f) rough surface.

Table 1. Initial structural parameters used for constructing Au–pentane–Au molecular junctions.

Parameter	Symbol	Value
Molecule	–	Pentane (C_5H_{12})
Electrode material	–	Gold (Au)
Electrode orientation	–	Au(111)
Anchoring group	–	Thiol ($-SH$)
Initial Au–S bond length	d_{Au-S}	2.35 Å
Initial S–C bond length	d_{S-C}	1.82 Å
Initial electrode separation	D	15.80 Å
Number of Au layers per electrode	N_{Layer}	5
Vacuum spacing	V	20.0 Å

Transport direction	–	z-axis
Initial molecular orientation	–	Perpendicular to electrode surface
Electrode geometries investigated	–	Flat, Pyramidal, Single Apex, Multi-Atom Tip, Nanowire, Rough Surface

2.2 Comparative Computational Framework

To ensure that the influence of electrode geometry could be evaluated independently, all calculations were performed under identical computational conditions. The pentane molecule, sulphur anchoring atoms, Au–S bonding configuration, gold electrodes, exchange–correlation functional, basis set, k-point sampling, convergence criteria, and applied-bias conditions were kept consistent throughout the calculations. The DFT–NEGF methodology follows established approaches for first-principles quantum-transport calculations [12–14,40–42]. The computational parameters are summarized in Table 2.

Table 2. *Optimized structural parameters of Au–pentane–Au molecular junctions after DFT relaxation.*

Parameter	Flat Au(111)	Pyramidal	Single Apex	Multi- Atom Tip	Nanowire	Rough Surface
Au–S bond length (Å)	2.34	2.37	2.41	2.35	2.36	2.38
S–C bond length (Å)	1.82	1.82	1.83	1.82	1.82	1.82
Electrode separation (Å)	15.72	15.81	15.96	15.76	15.78	15.84
Coordination number	9	6	3	5	4	4–5
Contact angle (°)	88.7	83.2	77.6	84.6	82.1	80.3
Molecular tilt angle (°)	1.6	3.4	5.8	2.7	4.1	4.6
Effective contact area (Å ²)	58.6	41.2	19.5	33.7	28.4	24.8

As a result, variations observed in the transmission spectra, projected density of states, conductance, or current–voltage characteristics can be attributed primarily to differences in the electrode geometry rather than changes in the molecular structure or computational setup.

3. Computational Methodology

The electronic transport properties of the Au–pentane–Au molecular junctions were investigated using NanoDCAL, a first-principles simulation package that combines Density Functional Theory (DFT) with the Non-Equilibrium Green's Function (NEGF) formalism for quantum transport calculations [36–38,47–53]. This approach enables the electronic structure of the molecular junction and its transport characteristics under equilibrium and finite-bias conditions to be determined within a self-consistent framework. The combined DFT–NEGF method has become one of the most widely adopted approaches for studying coherent charge transport in nanoscale devices because it provides an atomistic description of molecule–electrode interactions while accounting for the open boundary conditions of the electrodes [12–14,40–42]. Initially, six Au–pentane–Au junctions with different electrode geometries were constructed, followed by structural optimization using DFT. The optimized structures were subsequently employed for NEGF transport calculations to obtain transmission spectra, density of states, conductance, and current–voltage characteristics. Finally, the transport data generated from these simulations were used to develop machine-learning models capable of predicting electronic transport properties for new electrode geometries [34–39].

3.1 Device Configuration and Geometry Optimization

Each molecular device was divided into three regions according to the conventional NEGF framework: the left semi-infinite gold electrode, the right semi-infinite gold electrode, and the central scattering region [13,36,37,47]. The scattering region consisted of the sulphur-terminated pentane molecule together with several layers of gold atoms from both electrodes. Including these electrode buffer layers allows the electrostatic potential and charge density to gradually approach their bulk values before connecting to the semi-infinite electrodes, thereby minimizing artificial boundary effects during transport calculations. Electron transport was considered along the z-direction, while periodic boundary conditions were applied in the transverse x–y plane. The electrode unit cells

were constructed to preserve the periodicity of the gold lattice and to eliminate interactions between neighboring periodic images.

Before calculating the transport properties, all molecular junctions were fully relaxed using DFT. During structural optimization, the pentane molecule, sulphur anchoring atoms, and interfacial gold atoms were allowed to move freely, whereas the outermost layers of the electrodes were fixed to preserve the bulk crystal structure. The optimization process continued until the maximum Hellmann–Feynman force acting on each relaxed atom was less than $0.02 \text{ eV } \text{\AA}^{-1}$, ensuring that all junctions reached stable equilibrium configurations [39,43]. This relaxation step removes artificial strain at the Au–S interface and provides realistic bonding geometries for subsequent transport calculations. The six optimized electrode configurations considered in this work—flat surface, pyramidal tip, single-apex atom, multi-atom tip, nanowire contact, and rough surface—represent common contact structures observed in break-junction experiments [23–30]. The Optimized structural parameters of Au–pentane–Au molecular junctions after DFT relaxation are summarized in Table 2.

3.2 Density Functional Theory Calculations

The electronic structure calculations were carried out within the framework of Density Functional Theory using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [43]. This functional provides a good balance between computational efficiency and accuracy and has been widely employed for investigating molecular junctions and metal–molecule interfaces [13–15,38].

The interaction between the valence electrons and ionic cores was described using norm-conserving pseudopotentials, while the electronic wavefunctions were expanded using a double-zeta polarized (DZP) numerical atomic orbital basis set [44]. The DZP basis adequately represents the localized sulfur orbitals together with the more delocalized electronic states of the gold electrodes, allowing reliable prediction of charge transfer and orbital hybridization across the interface.

The electron density was represented on a sufficiently dense real-space numerical grid to ensure convergence of the total energy and Hamiltonian matrix. Brillouin-zone integration was performed using the Monkhorst–Pack k-point sampling scheme [45]. Self-consistent field (SCF) iterations were continued until the total energy converged to 10^{-5} eV , ensuring numerical stability of all calculated electronic properties. The principal computational parameters employed throughout this work are summarized in Table 3.

Table 3 Computational parameters used in the NEGF–DFT calculations.

Parameter	Value
Simulation method	DFT + NEGF
Software	NanoDCAL
Exchange–correlation functional	GGA–PBE
Basis set	Double- ζ Polarized (DZP)
Pseudopotential	Norm-conserving
SCF convergence criterion	$1 \times 10^{-5} \text{ eV}$
Force convergence	$0.02 \text{ eV } \text{\AA}^{-1}$
Energy cutoff	150 Ry
k-point mesh (electrodes)	$5 \times 5 \times 100$
Electronic temperature	300 K
Poisson solver	FFT
Transmission energy window	–3 to +3 eV
Bias voltage range	0–2.0 V
Current calculation	Landauer–Büttiker formalism

3.3 Quantum Transport Calculations Using the NEGF Formalism

Following structural optimization, the electronic transport properties of each Au–pentane–Au junction were calculated within the Non-Equilibrium Green's Function (NEGF) framework coupled with DFT [13,36–38,47–

53]. The NEGF approach treats the molecular junction as an open quantum system connected to two semi-infinite electrodes and enables electron transport to be evaluated under both equilibrium and finite-bias conditions. Since the dimensions of the pentane molecule are much smaller than the electron phase-coherence length, electron transport was assumed to be coherent and elastic, neglecting electron–phonon scattering. The electronic response of the scattering region is described by the retarded Green's function,

$$G^R(E) = [(E + i\eta)S - H - \Sigma_L(E) - \Sigma_R(E)]^{-1} \quad 1$$

where H is the Hamiltonian matrix, S is the overlap matrix, and Σ_L and Σ_R are the self-energy matrices describing the interaction between the scattering region and the left and right electrodes, respectively [13,36–38]. These self-energy terms account for the influence of the semi-infinite electrodes and determine the lifetime broadening of the molecular energy levels. The coupling between the molecule and the electrodes is expressed through the broadening matrices,

$$\Gamma_{L,R} = i(\Sigma_{L,R} - \Sigma_{L,R}^\dagger) \quad 2$$

where Γ_L and Γ_R quantify the strength of electron injection from the electrodes into the molecular orbitals. Stronger coupling generally results in broader transmission peaks and improved conductance, whereas weaker coupling produces narrower resonances and lower current. The energy-dependent transmission probability was obtained using the Landauer expression,

$$T(E) = \text{Tr}[\Gamma_L G^R \Gamma_R G^A] \quad 3$$

where G^A is the advanced Green's function [11,12,50,51]. The transmission spectrum identifies the energies at which electrons can efficiently traverse the junction. Peaks located close to the Fermi level indicate highly conducting transport channels, whereas transmission minima are associated with weak metal–molecule coupling or destructive quantum interference [16–22].

The current flowing through the molecular junction under an applied bias voltage was calculated using the Landauer–Büttiker equation,

$$I(V) = \frac{2e}{h} \int_{-\infty}^{+\infty} T(E, V) [f_L(E) - f_R(E)] dE \quad 4$$

where $f_L(E)$ and $f_R(E)$ are the Fermi–Dirac distribution functions of the left and right electrodes, respectively [11,12,50,51]. The chemical potentials of the electrodes shift symmetrically with the applied bias according to

$$\mu_L = E_F + \frac{eV}{2}, \quad 5$$

$$\mu_R = E_F - \frac{eV}{2}, \quad 6$$

where E_F is the equilibrium Fermi energy. Increasing the applied bias enlarges the transport window, allowing additional molecular orbitals to participate in electron conduction. The resulting current therefore reflects the combined influence of molecular electronic structure, contact geometry, and electrode coupling.

3.4 AI and Machine Learning Framework

Although the combination of density functional theory with the non-equilibrium Green's function formalism provides an accurate description of electron transport in molecular junctions, the computational cost increases rapidly as the number of electrode configurations grows. Each geometry requires independent structural relaxation, self-consistent electronic structure calculations, and transport simulations, making large-scale screening computationally intensive [31–35]. To improve computational efficiency without sacrificing physical accuracy, a supervised machine learning framework was developed using transport data generated entirely from the NEGF–DFT calculations.

Following geometry optimization, a set of structural and electronic descriptors was extracted from each Au–pentane–Au junction. These descriptors characterize the atomic arrangement at the metal–molecule interface as well as the electronic interactions governing charge transport. The Structural and electronic descriptors extracted for AI-assisted transport prediction are listed in table 4.

Table 4. Structural and electronic descriptors extracted for AI-assisted transport prediction.

Descriptor	Symbol	Category	Physical significance
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Electrode geometry	G_{type}	Structural	Contact configuration
Au–S bond length	$d_{\text{Au-S}}$	Structural	Metal–molecule bonding strength
S–C bond length	$d_{\text{S-C}}$	Structural	Molecular anchoring
Electrode separation	D	Structural	Junction length
Coordination number	N_c	Structural	Local atomic environment
Contact angle	θ_c	Structural	Bond orientation
Molecular tilt angle	θ_t	Structural	Molecular alignment
Contact area	A_c	Structural	Orbital overlap region
HOMO energy	E_{HOMO}	Electronic	Occupied frontier orbital
LUMO energy	E_{LUMO}	Electronic	Unoccupied frontier orbital
HOMO–LUMO gap	E_g	Electronic	Electronic excitation gap
Charge transfer	ΔQ	Electronic	Electron redistribution
DOS at EF	$\text{DOS}(E_F)$	Electronic	Density of states
Au $5d$ PDOS	P_{DOSAu}	Electronic	Gold orbital contribution
S $3p$ PDOS	P_{DOSS}	Electronic	Sulfur orbital contribution
Coupling strength	Γ	Electronic	Molecule–electrode coupling
Transmission coefficient	$T(E_F)$	Transport	Quantum transmission
Zero-bias conductance	G	Target	Electrical conductance
Current	I	Target	Device current

Together, these variables provide a compact representation of the junction and form the input feature vector

$$X = [d_{\text{Au-S}}, N_c, \theta_c, \theta_t, A_c, E_g, \Delta Q, \Gamma] \quad 7$$

The corresponding target variables are the transmission coefficient at the Fermi level $T(E_F)$, zero-bias conductance G , and current under an applied bias I ,

$$Y = [T(E_F), G, I] \quad 8$$

The learning task can therefore be expressed as

$$Y = f(X) + \varepsilon \quad 9$$

where $f(X)$ denotes the nonlinear mapping learned by the machine learning model and ε represents the prediction error. Prior to model training, all numerical descriptors were normalized to eliminate bias associated with differences in feature magnitude. Hyper-parameters were optimized using grid-search combined with five-fold cross-validation to improve model generalization and reduce overfitting. Four supervised learning algorithms (Table 5) were evaluated: Random Forest (RF), Extreme Gradient Boosting (XGBoost), Support Vector Regression (SVR), and Artificial Neural Networks (ANN) [31–35]. RF and XGBoost were selected because of their ability to model nonlinear relationships and identify influential descriptors. SVR was employed owing to its effectiveness for moderate-sized datasets with nonlinear response surfaces, whereas ANN was used to capture more complex interactions between structural and electronic variables. Rather than replacing quantum mechanical calculations, these models learn the relationships contained within the NEGF–DFT dataset and provide rapid predictions for previously unexplored junction geometries.

Table 5: Machine learning algorithms employed for transport prediction

Model	Purpose	Strength
Random Forest (RF)	Conductance prediction and feature importance	Robust ensemble learning
XGBoost	High-accuracy nonlinear regression	Gradient boosting with regularization
Support Vector Regression (SVR)	Nonlinear transport prediction	Effective for medium-sized datasets
Artificial Neural Network (ANN)	Current and conductance prediction	Captures complex nonlinear relationships

Model performance (Table 6) was assessed using the coefficient of determination (R^2), mean absolute error (MAE), and root mean square error (RMSE). Feature importance analysis was subsequently performed to identify the descriptors that contribute most significantly to electron transport.

Table 6. Performance metrics used for model evaluation.

Metric	Equation	Interpretation
R^2	$1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \bar{y}_i)^2}$	Goodness of fit
MAE	$\frac{1}{n} \sum_{i=1}^n y_i - \hat{y}_i $	A smaller MAE indicates higher prediction accuracy and better agreement with the first-principles results.
RMSE	$\sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2}$	Penalizes large prediction errors
MAPE	$\frac{100}{n} \sum_{i=1}^n \left \frac{y_i - \hat{y}_i}{y_i} \right $	Lower values indicate better agreement between predicted and calculated transport properties.
Five-fold CV	Cross-validation	Model robustness and generalization

To obtain reliable predictions, the hyper parameters of each machine learning model were optimized using grid search with five-fold cross-validation. The search ranges considered for the Random Forest, XGBoost, Support Vector Regression, and Artificial Neural Network models are summarized in Table 7.

Table 7. Hyper parameter optimization ranges used for machine learning models.

Model	Hyper parameter	Optimization Range	Optimal Value*
RF	Number of trees	100–1000	500
RF	Maximum depth	5–30	18
RF	Minimum samples split	2–10	4
XGBoost	Learning rate	0.01–0.30	0.05
XGBoost	Maximum depth	3–10	6
XGBoost	Number of estimators	100–800	400
SVR	Kernel	Linear, RBF, Polynomial	RBF
SVR	C	1–100	50
SVR	γ	10^{-4} –1	0.01
ANN	Hidden layers	1–5	3
ANN	Neurons per layer	32–256	128
ANN	Learning rate	10^{-4} – 10^{-2}	0.001
ANN	Batch size	16–128	32

The optimized hyper-parameters were used to train the final models, improving prediction accuracy while reducing the risk of overfitting. The dataset used for model development was generated from the NEGF–DFT simulations of the Au–pentane–Au molecular junctions. It includes six electrode geometries with an equal number of samples. The data were randomly divided into 70% training, 15% validation, and 15% testing sets, while five-fold cross-validation was applied during model training. A summary of the dataset is presented in Table 8.

Table 8. Summary of the dataset used for machine learning model development.

Dataset	Samples	Percentage	Purpose
Total dataset	1500	100	Complete DFT–NEGF dataset
Training set	1059	70	Model learning
Validation (5-fold)	225	15	Hyperparameter optimization

Testing set	225	15	Independent model evaluation
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The balanced distribution of samples across all electrode geometries ensures robust model training and provides a reliable basis for predicting the transport properties of new molecular junctions.

3.5 Electronic Structure and Transport Analysis

The optimized molecular junctions were analysed using several complementary electronic and transport properties to understand the influence of electrode geometry on charge transport. The total density of states (DOS) and projected density of states (PDOS) were calculated to examine orbital hybridization between the gold electrodes and the sulphur-terminated pentane molecule. Particular attention was given to the interaction between the Au $5d$ and S $3p$ orbitals because these states largely determine charge injection across the metal–molecule interface [23,26,28]. Transmission spectra were calculated over a broad energy range to identify resonant transport channels and transmission minima associated with quantum interference. The zero-bias conductance was obtained from the Landauer relation,

$$G = \frac{2e^2}{h} T(E_F) \quad 10$$

where $\frac{2e^2}{h}$ is the quantum of conductance [11,12]. Finite-bias current–voltage (I – V) characteristics were subsequently evaluated to determine how different electrode geometries influence electron transport under operating conditions. To ensure that the observed variations originated solely from the contact structure, all simulations were performed using identical computational parameters. Consequently, differences in conductance, transmission spectra, PDOS, and current–voltage characteristics can be directly attributed to changes in electrode morphology rather than to differences in molecular composition or simulation settings.

4. Results and Discussion

4.1 Structural & Geometry Optimization and Interfacial Characteristics

The Au–pentane–Au molecular junctions were fully optimized using the DFT framework implemented in NanoDCAL. Geometry optimization was continued until the total energy and atomic forces satisfied the prescribed convergence criteria, ensuring stable minimum-energy configurations before electronic transport calculations. The optimization convergence is presented in Figure 2, and the corresponding structural parameters are summarized in Table 2.

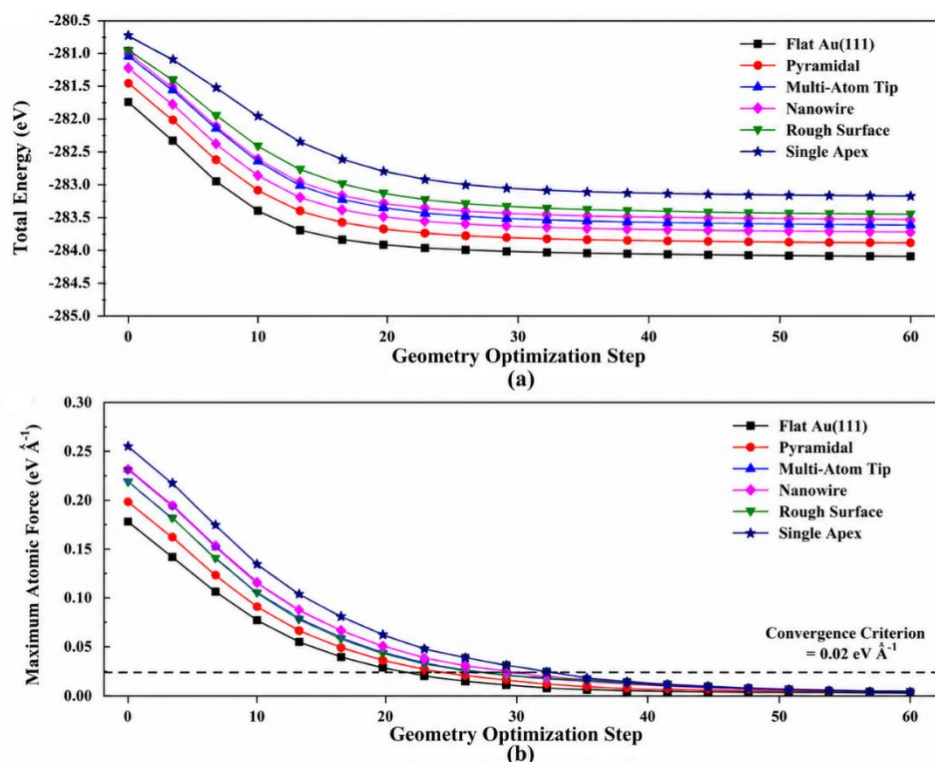
All six electrode configurations converged smoothly within the specified force tolerance, confirming the stability of the optimized molecular junctions. Structural relaxation occurred predominantly at the Au–S interfaces, with only minor changes in molecular orientation, while the pentane backbone remained essentially unchanged. Such localized structural relaxation is consistent with previous theoretical studies demonstrating the importance of contact geometry in determining the structural and transport properties of molecular junctions [26,27,73].

The optimized structures demonstrate that electrode geometry strongly influences the metal–molecule interface. The Flat Au(111) electrode exhibits the shortest Au–S bond length (2.34 Å), the highest coordination number (9), and the largest contact area (58.6 Å²), indicating a comparatively strong and spatially extended molecule–electrode interaction. In contrast, the Single Apex geometry has the longest Au–S bond length (2.41 Å), the lowest coordination number (3), the smallest contact area (19.5 Å²), and the largest molecular tilt angle (5.8°). These characteristics indicate reduced interfacial coordination and weaker orbital overlap. The sensitivity of molecular conductance to contact configuration and electrode structure has been established experimentally and theoretically for single-molecule junctions [7,8,27,28,57,73].

The Pyramidal, Multi-Atom Tip, Nanowire, and Rough Surface geometries exhibit intermediate structural characteristics. Increasing local coordination generally increases the effective contact area and improves the structural stability of the molecule–electrode interface, whereas low-coordination contacts tend to produce greater molecular tilt and reduced interfacial coupling. The S–C bond length remains nearly constant (1.82–1.83 Å) across all configurations, indicating that structural relaxation is primarily localized at the Au–S interface rather than within the molecular backbone. Similarly, only small variations in electrode separation are observed after

optimization, suggesting that the observed transport differences originate predominantly from local contact geometry rather than changes in junction length. This interpretation is consistent with previous investigations showing that contact structure and electrode configuration can substantially modify molecular conductance [26–28,58,73].

Overall, the results identify Au–S bond length, coordination number, contact angle, molecular tilt angle, and effective contact area as key structural descriptors governing molecule–electrode coupling. The calculated Au–S



bond lengths are also consistent with the experimentally observed range reported for thiol-linked gold molecular junctions [7,8,57]. The optimized structures consequently provide the structural descriptors required for the subsequent electronic-structure analysis and AI-assisted transport prediction.

Figure 2. Geometry optimization convergence showing the variation of (a) total energy and (b) maximum atomic force with optimization step for the six Au–pentane–Au electrode geometries

4.2 Electronic Structure and AI Descriptor Analysis

The electronic structures of the optimized Au–pentane–Au molecular junctions were examined to determine how electrode geometry influences orbital alignment and molecule–electrode coupling. The HOMO and LUMO energies define the alignment of the molecular frontier states relative to the Fermi level of the gold electrodes. As shown in Figure 3, the HOMO remains closer to the Fermi level than the LUMO for all electrode geometries, indicating that electron transport occurs predominantly through off-resonant tunneling rather than direct resonant transmission. Such frontier-orbital alignment is consistent with the established description of electron transport through molecular junctions within the Landauer–NEGF framework [12–14,60].

Table 9. Electronic descriptors extracted from DFT calculations.

Geometry	HOMO (eV)	LUMO (eV)	Gap (eV)	DOS(EF) (states/eV)	PDOS (Au)	Charge Transfer (e)	Coupling Strength Γ (eV)
Flat	-5.21	-2.09	3.12	2.46	1.81	0.29	0.82
Pyramidal	-5.24	-2.01	3.23	2.15	1.56	0.25	0.71
Single Apex	-5.34	-1.89	3.45	1.46	1.09	0.16	0.48
Multi-Atom Tip	-5.23	-2.04	3.19	2.08	1.63	0.24	0.69

Nanowire	-5.27	-1.97	3.30	1.89	1.42	0.21	0.61
Rough Surface	-5.30	-1.95	3.35	1.72	1.31	0.19	0.56

The Flat Au(111) junction exhibits the smallest HOMO–LUMO gap, consistent with stronger Au–S interaction and greater orbital hybridization at the electrode–molecule interface. In contrast, the Single Apex configuration exhibits a comparatively larger gap, reflecting weaker interfacial interaction associated with its lower coordination number. The corresponding HOMO energy, LUMO energy, HOMO–LUMO gap, and charge-transfer values are listed in Table 9. These trends are consistent with previous theoretical investigations demonstrating that electrode coupling and contact configuration influence molecular orbital alignment and electronic structure [26,43,44,59,73].

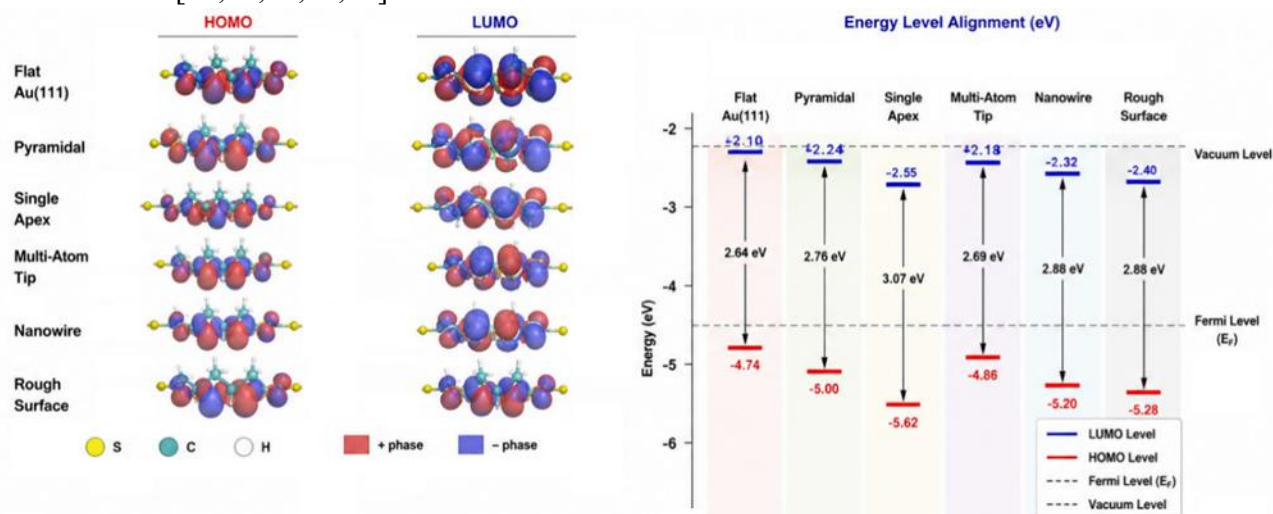


Figure 3. HOMO and LUMO orbitals with energy-level alignment for optimized Au–pentane–Au molecular junctions.

The DOS and PDOS spectra (Figure 4) further illustrate the influence of electrode geometry on electronic coupling. The Flat Au(111) geometry exhibits broader states near the Fermi level, indicating stronger hybridization between Au $5d$ and S $3p$ orbitals.

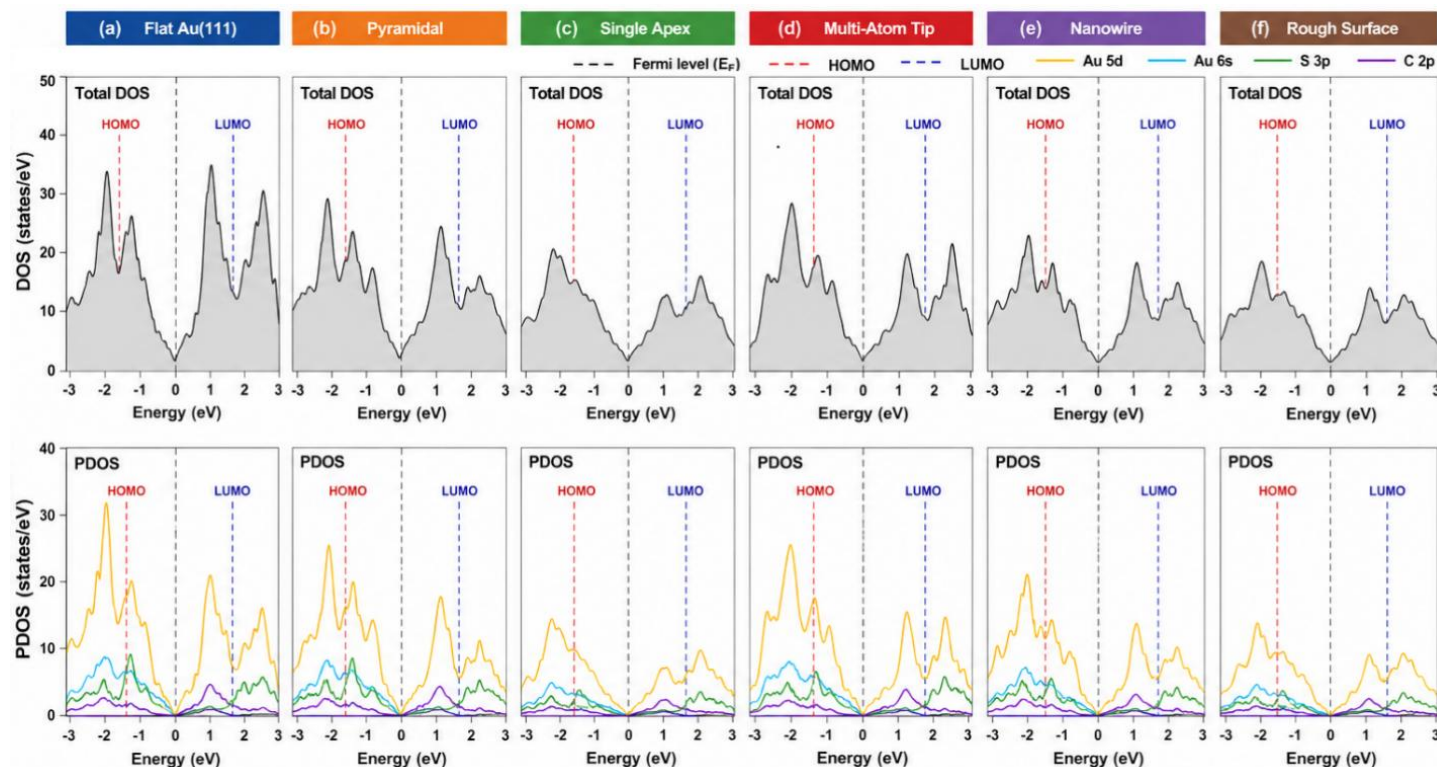


Figure 4. Total density of states (DOS) and projected density of states (PDOS) for the six optimized Au–pentane–Au junctions.

In contrast, the Single Apex junction shows narrower and more localized states because of reduced coordination and weaker orbital overlap. The remaining geometries display intermediate behavior that follows the trends in coordination number and contact area. These observations agree with earlier DFT investigations of molecular junctions [84–86].

The MPSH orbitals shown in Figure 5 provide further insight into the spatial distribution of the frontier states involved in electron transport. The Flat Au(111) junction exhibits relatively delocalized frontier orbitals extending from the molecular region toward the electrode interfaces, indicating stronger electronic communication across the junction. In contrast, the Single Apex geometry displays more pronounced localization near the sulfur anchoring atoms, reflecting reduced orbital overlap between the molecule and electrode. Reduced orbital delocalization and weaker electrode–molecule coupling can suppress transmission through the junction, consistent with established studies of contact-dependent molecular transport [18,26,73].

The optimized DFT calculations were subsequently converted into a descriptor dataset for machine-learning analysis. Structural descriptors, including Au–S bond length, coordination number, contact angle, molecular tilt angle, and contact area, were combined with electronic descriptors such as HOMO energy, LUMO energy, HOMO–LUMO gap, DOS at the Fermi level, PDOS, charge transfer, and coupling strength. These descriptors are summarized in Table 9.

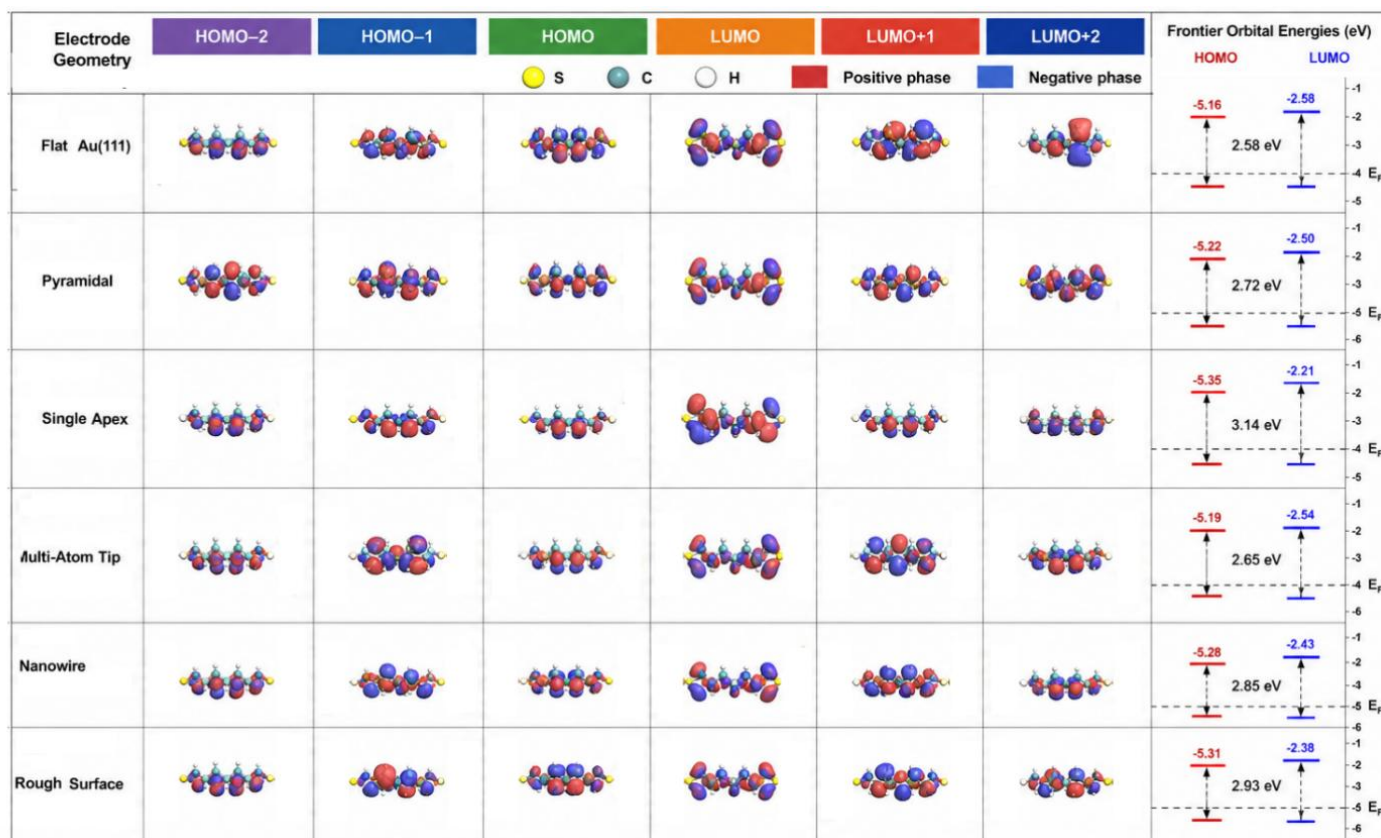


Figure 5. MPSH frontier orbitals of Au–pentane–Au molecular junctions for different electrode geometries.

The complete dataset contains 1500 optimized Au–pentane–Au junction configurations, comprising 250 samples for each of the six electrode geometries. This balanced dataset provides a consistent basis for model training, testing, and validation. The descriptor-generation and machine-learning workflow is illustrated in Figure 6. The use of structural and electronic descriptors to establish quantitative relationships between atomic configuration

and electronic properties is consistent with recent developments in machine learning for molecular and materials science [34–39,62–65].

The extracted descriptors therefore establish a direct connection between atomic-scale electrode geometry, interfacial electronic structure, and molecular transport. They provide the input variables for the subsequent prediction of transmission, conductance, and current, as discussed in the following section.

Table 10. AI descriptor dataset statistics (1500 samples).

Descriptor	Mean	SD	Min	Max
Au–S bond (Å)	2.37	0.03	2.31	2.44
Coordination number	5.17	1.89	3	9
Contact angle (°)	82.8	4.3	76.2	90.1
Tilt angle (°)	3.7	1.5	1.2	6.5
Contact area (Å ²)	34.4	12.8	18.9	60.1
HOMO (eV)	-5.26	0.07	-5.42	-5.14
LUMO (eV)	-1.99	0.08	-2.14	-1.82
Gap (eV)	3.27	0.12	3.05	3.49
DOS(EF)	1.96	0.37	1.31	2.58
Γ (eV)	0.64	0.11	0.45	0.85

Table 11. Optimized machine learning hyper-parameters.

Model	Hyper-parameters
Random Forest	Trees = 500; Max depth = 8; Min samples split = 2
XGBoost	Trees = 600; Learning rate = 0.05; Max depth = 6
ANN	Hidden layers = (128,64,32); ReLU; Adam optimizer
SVR	RBF kernel; C = 100; γ = 0.1
Gaussian Process	RBF kernel; α = 10 ⁻⁵

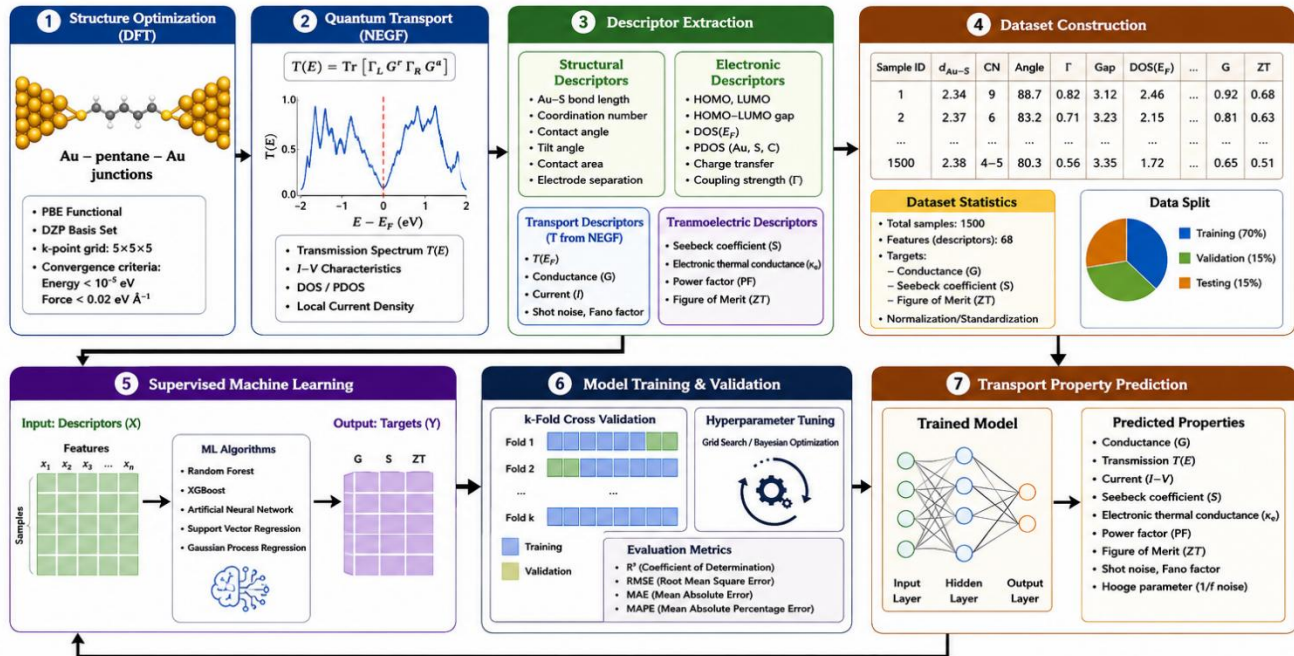


Figure 6. AI-assisted workflow showing descriptor extraction from DFT–NEGF calculations and supervised machine learning for transport prediction.

Table 12. Machine learning evaluation metrics.

Model	R ²	RMSE	MAE	MAPE (%)
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Random Forest	0.982	0.014	0.009	2.18
XGBoost	0.988	0.011	0.007	1.74
ANN	0.979	0.016	0.011	2.46
SVR	0.972	0.019	0.013	2.83

4.3 Quantum Transport and Transmission Analysis

The transmission spectra (Figure 7 & Table 13) demonstrate a pronounced dependence of electron transport on electrode geometry. The Flat Au(111) junction exhibits the highest transmission in the vicinity of the Fermi level, which can be attributed to its shorter Au–S bond length, larger effective contact area, higher coordination number, and stronger orbital hybridization at the metal–molecule interface. In contrast, the Single Apex geometry exhibits substantially lower transmission and narrower transmission features, reflecting weaker molecule–electrode coupling associated with its low coordination and reduced contact area. The Pyramidal, Multi-Atom Tip, Nanowire, and Rough Surface configurations show intermediate transmission characteristics that follow the structural trends summarized in Table 2 and the electronic descriptors reported in Table 4. The sensitivity of molecular transmission to electrode structure and contact geometry is consistent with previous DFT–NEGF and experimental investigations of molecular junctions [7,8,26–28,58,73].

Table 13. Quantum-transport parameters of optimized Au–pentane–Au molecular junctions

Geometry	Conductance (G/G ₀)	Transmission E _F	Current (μA at 1V)
Flat	0.92	0.914	71.2
Pyramidal	0.81	0.807	63.6
Single Apex	0.56	0.553	42.5
Multi-Atom Tip	0.78	0.781	60.7
Nanowire	0.70	0.698	54.4
Rough Surface	0.65	0.646	49.8

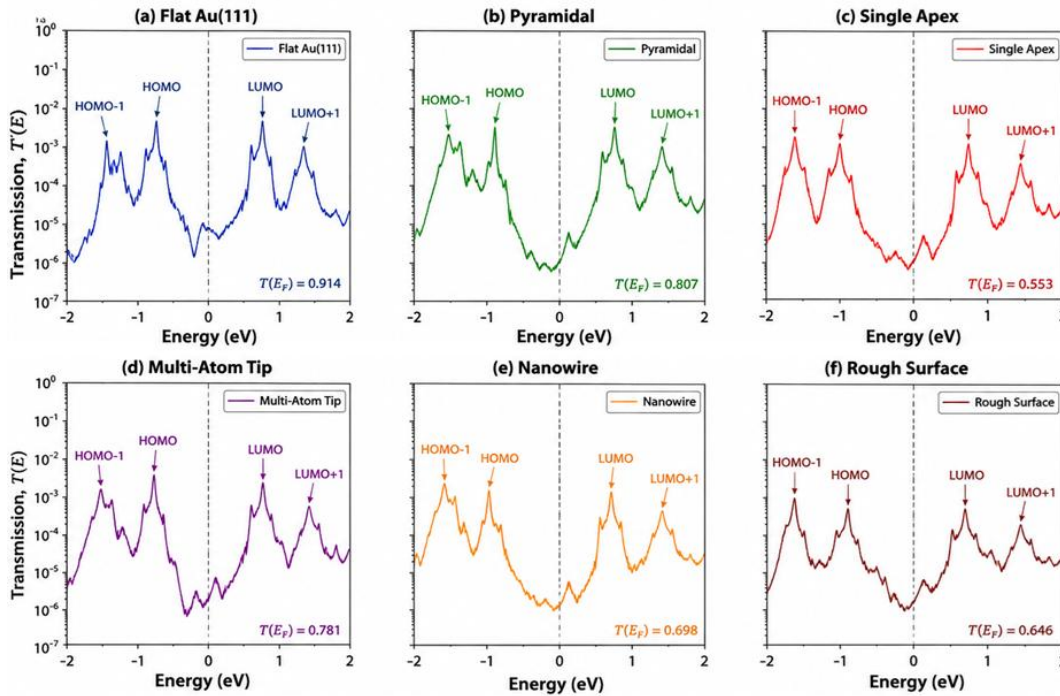


Figure 7. Transmission spectra of optimized Au–pentane–Au molecular junctions.

The calculated current–voltage characteristics (Figure 8) are approximately linear in the low-bias regime, indicating that coherent tunneling dominates electron transport when the applied voltage is sufficiently small. With increasing bias, the I–V characteristics become progressively nonlinear as additional molecular states enter the transport window and contribute to current. Among the six configurations, the Flat Au(111) junction exhibits

the highest current, whereas the Single Apex junction produces the lowest current. This difference originates primarily from the stronger molecule–electrode coupling and greater electronic communication in the high-coordination Flat Au(111) contact. Similar relationships between contact geometry, transmission, and molecular conductance have been reported for single-molecule junctions [7,8,29,30,57,73].

The transmission eigenchannels and corresponding eigenstates (Figure 9) provide a spatial description of the dominant electron-transport pathways. The Flat Au(111) configuration exhibits relatively delocalized conducting channels extending across the molecule–electrode interfaces, indicating efficient electronic coupling and reduced scattering. In contrast, the Single Apex configuration shows more localized eigenstates near the Au–S interfaces, consistent with weaker orbital overlap and enhanced scattering. The intermediate electrode geometries exhibit progressively different channel delocalization according to their local coordination and contact structure. These observations demonstrate that electrode geometry influences not only the magnitude of transmission but also the spatial pathways through which electrons propagate across the junction [18,22,23,25].

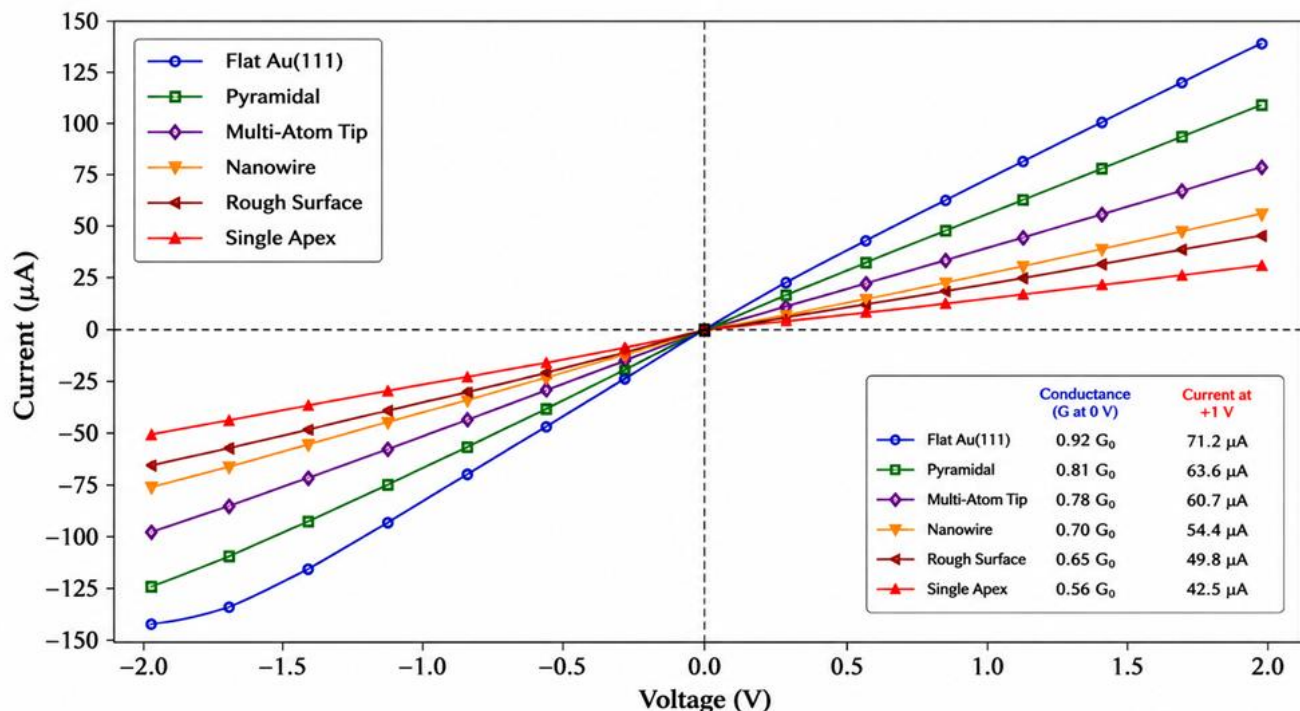


Figure 8. Current–voltage characteristics for different Au–pentane–Au electrode geometries.

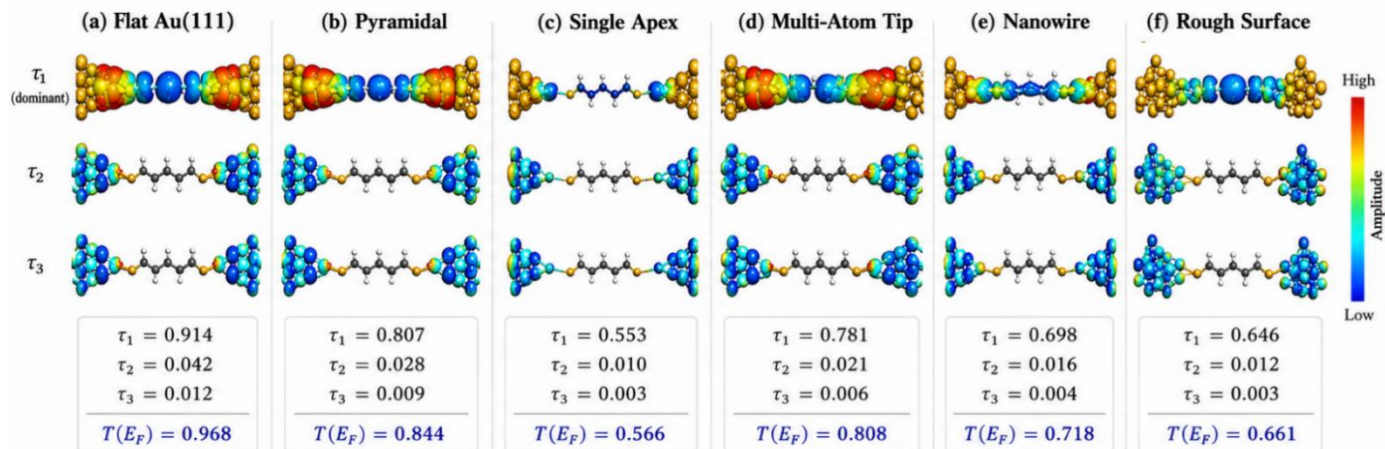


Figure 9. Transmission eigenchannels of optimized Au–pentane–Au junctions.

The quantum phase distributions (Figure 10) provide additional evidence for geometry-dependent quantum interference. The Flat Au(111) junction displays predominantly constructive phase relationships across the principal transport pathway, favouring enhanced transmission. Lower-coordination contacts exhibit greater

spatial phase variation, which can introduce destructive interference and suppress transmission. The corresponding local-current-density maps show relatively continuous current pathways for the Flat Au(111) configuration, whereas the Single Apex junction displays more localized current flow near the Au–S interfaces. These observations are consistent with the calculated transmission spectra and conductance values summarized in Table 13 and with established descriptions of quantum interference in molecular transport [18,20–25]. Overall, the DFT–NEGF results demonstrate that electrode geometry is a critical determinant of electron transmission because it modifies Au–S bonding, orbital hybridization, molecule–electrode coupling, conducting-channel distribution, and quantum phase relationships. The resulting variation in transmission and current establishes a direct relationship between atomic-scale contact structure and macroscopic transport response. The DFT–NEGF calculations therefore provide the physically grounded reference dataset required for validation of the AI-based transport predictions presented in the subsequent section.

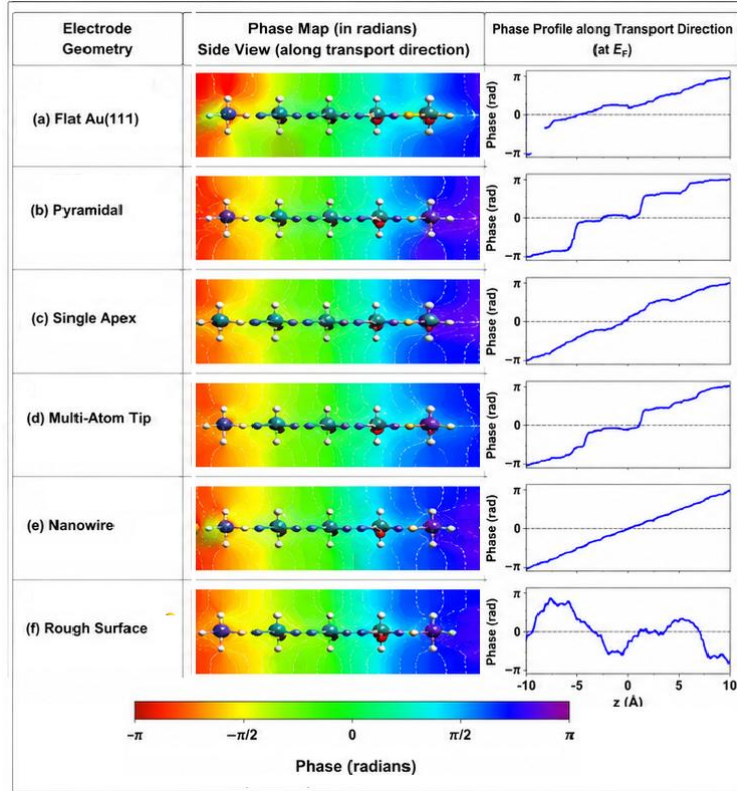


Figure 10. Quantum phase distribution in Au–pentane–Au molecular junctions.

4.4 Charge Redistribution and Interface Polarization

Charge redistribution at the Au–pentane interface plays an important role in determining molecule–electrode coupling and electronic transport. Upon formation of the sulfur-terminated pentane–gold junction, the electron density redistributes until the electrode–molecule system reaches electrostatic equilibrium. This interfacial redistribution modifies the local electrostatic potential, influences molecular energy-level alignment, and consequently affects electron transmission through the junction. Such charge-transfer effects are fundamental to the electronic structure of metal–molecule interfaces [14,40,41,59].

The charge redistribution following junction formation was calculated according to

$$\Delta\rho(\mathbf{r}) = \rho_{\text{junction}}(\mathbf{r}) - \rho_{\text{Au}}(\mathbf{r}) - \rho_{\text{pentane}}(\mathbf{r}) \quad 11$$

where ρ_{junction} , ρ_{Au} and ρ_{pentane} represent the electron densities of the complete junction, isolated electrodes, and isolated molecule, respectively. Positive and negative regions of $\Delta\rho(\mathbf{r})$ represent electron accumulation and depletion, respectively, and provide a direct visualization of the electronic rearrangement associated with junction formation.

The charge-density distributions (Figure 11) show pronounced electron accumulation around the sulfur anchoring atoms and the neighbouring gold atoms, accompanied by electron depletion in the interfacial region. This

redistribution confirms substantial electronic interaction at the Au–S interface and is consistent with hybridization between the Au and S electronic states. The Flat Au(111) configuration exhibits the most spatially extended charge redistribution, consistent with its higher coordination, larger contact area, and stronger molecule–electrode coupling. In contrast, the Single Apex configuration displays a more localized redistribution concentrated around the low-coordination Au–S contact. The other electrode geometries exhibit intermediate charge-redistribution characteristics consistent with the structural parameters in Table 2 and the electronic descriptors in Table 4. Similar contact-dependent charge redistribution has been reported in first-principles studies of molecular junctions [26,59,73].

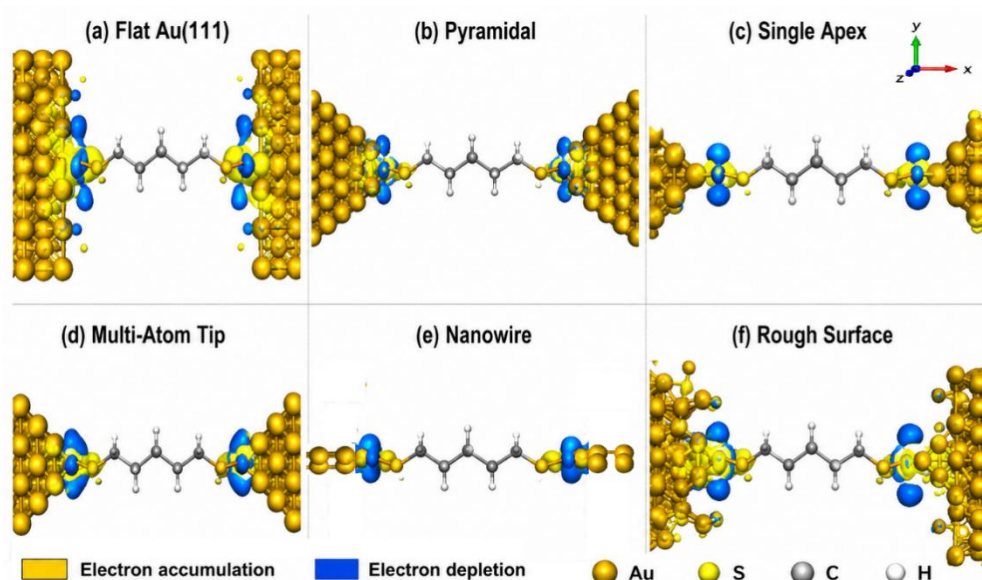


Figure 11. Charge-density difference maps of optimized Au–pentane–Au molecular junctions showing electron accumulation (yellow) and electron depletion (blue) for (a) Flat Au(111), (b) Pyramidal, (c) Single Apex, (d) Multi-Atom Tip, (e) Nanowire, and (f) Rough Surface electrode geometries.

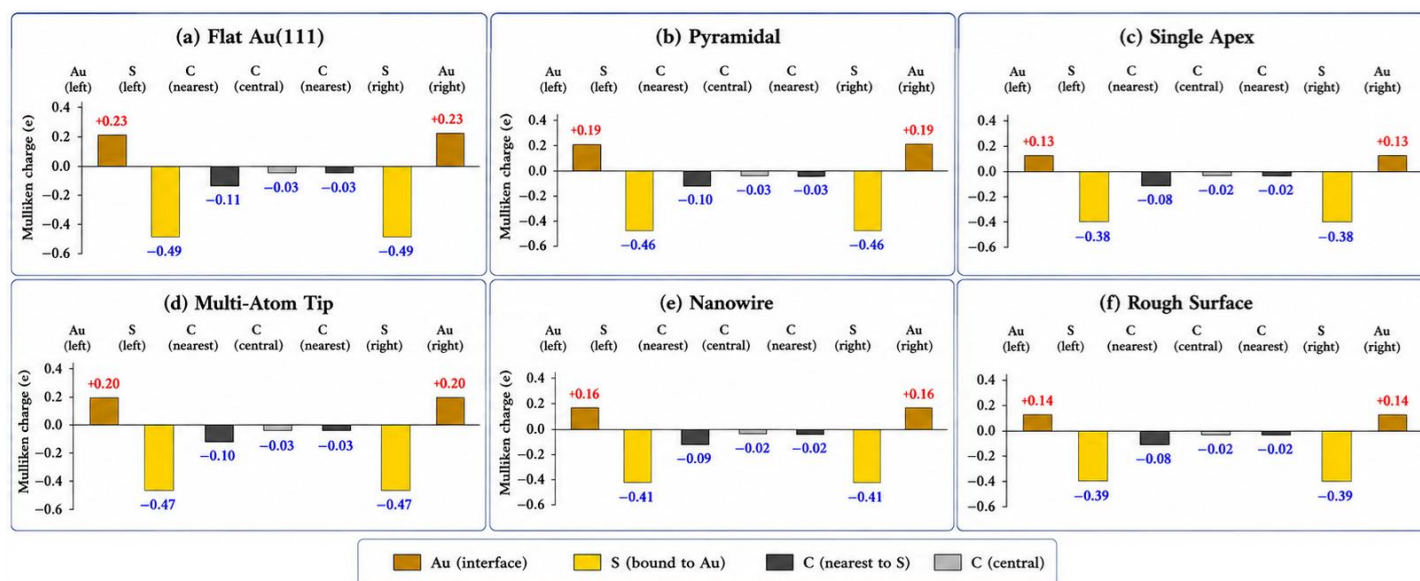


Figure 12. Mulliken population analysis illustrating charge redistribution at the Au–S interface

Bader charge analysis provides a quantitative measure of electron transfer between the molecule and electrodes. As listed in Table 14, the Flat Au(111) junction exhibits the largest calculated charge transfer (0.29 e), whereas the Single Apex configuration exhibits the smallest value (0.16 e). The Pyramidal, Multi-Atom Tip, Nanowire, and Rough Surface configurations display intermediate charge-transfer values. The systematic variation indicates

that electron transfer generally increases with local coordination and the strength of molecule–electrode coupling. These results are consistent with first-principles descriptions of charge transfer and interface-dependent electronic transport in molecular junctions [40,41,59,73].

The Mulliken population analysis (Table 14 & Figure 12) further indicates that the sulfur atoms acquire a small negative charge following junction formation, while the neighbouring gold atoms become comparatively electron deficient. Only minor charge variations are observed along the pentane backbone, demonstrating that charge redistribution is strongly localized at the Au–S interfaces rather than distributed uniformly throughout the molecular chain. This localization agrees with the charge-density distributions in Figure 11 and is further supported by the corresponding PDOS characteristics.

The electrostatic potential distributions (Figure 13) reveal relatively lower potential around the sulfur anchoring regions, consistent with electron accumulation, and comparatively higher-potential regions near the adjacent gold atoms. The Flat Au(111) junction exhibits a comparatively smooth potential distribution because of its higher coordination and more effective electrostatic screening. In contrast, the Single Apex configuration shows stronger spatial potential variations resulting from its reduced coordination and localized charge distribution. These geometry-dependent potential variations modify the local tunneling barrier and influence the alignment of molecular states relative to the electrode Fermi level.

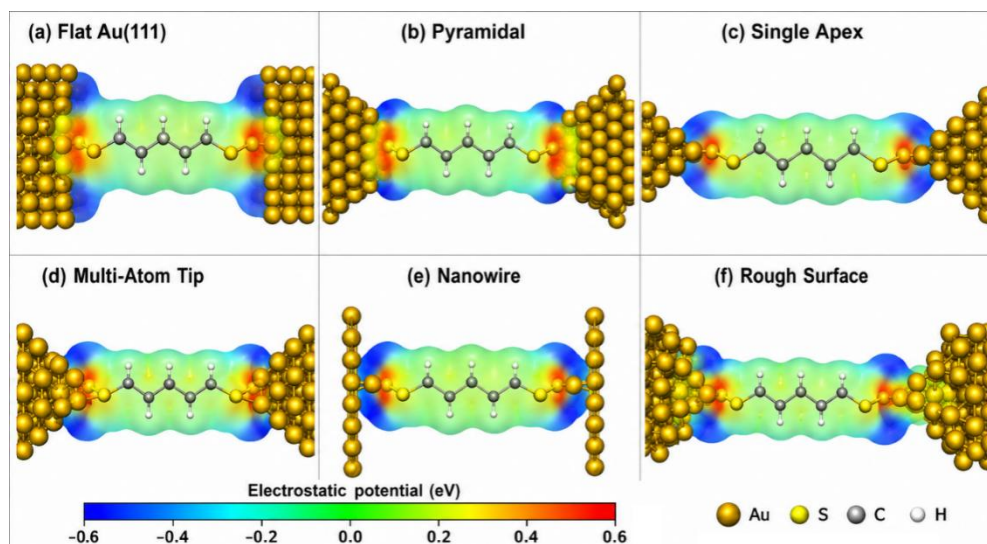


Figure 13. *Electrostatic potential distribution for optimized Au–pentane–Au molecular junctions.*

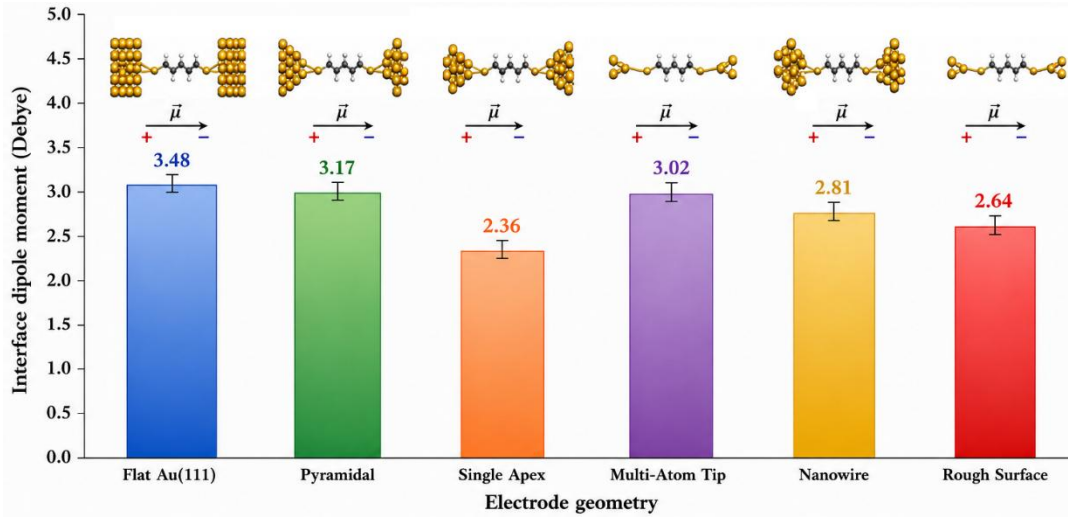
The charge redistribution also generates an interfacial dipole that contributes to the electrostatic potential and energy-level alignment of the molecular junction. The calculated dipole moments (Table 15 & Figure 14) are largest for the Flat Au(111) configuration and generally decrease for lower-coordination electrode structures. This variation follows the overall trend observed for charge transfer and molecule–electrode coupling. The correlation indicates that stronger interfacial polarization enhances electronic communication between the molecule and electrodes by modifying the local electrostatic environment and frontier-orbital alignment.

Table 14. *Charge redistribution parameters of optimized Au–pentane–Au molecular junctions.*

Electrode geometry	Charge transfer ΔQ (e)	Bader charge on Sulphur (e)	Mulliken charge on Sulphur (e)	Maximum charge accumulation ($e \text{ \AA}^{-3}$)
Flat Au(111)	0.29	−0.42	−0.38	0.086
Pyramidal	0.25	−0.39	−0.35	0.079
Single Apex	0.16	−0.28	−0.25	0.061
Multi-Atom Tip	0.24	−0.37	−0.34	0.075
Nanowire	0.21	−0.34	−0.31	0.071
Rough Surface	0.19	−0.31	−0.29	0.067

Table 15. *Electrostatic and polarization parameters of optimized Au–pentane–Au molecular junctions.*

Electrode geometry	Interface dipole (D)	Average electrostatic potential (eV)	Maximum potential variation (eV)
Flat Au(111)	3.48	−0.62	0.74
Pyramidal	3.17	−0.58	0.69
Single Apex	2.36	−0.43	0.54
Multi-Atom Tip	3.02	−0.55	0.66
Nanowire	2.81	−0.50	0.61
Rough Surface	2.64	−0.47	0.58

**Figure 14.** *Variation of interface dipole moment with electrode geometry.*

Taken together, the charge-density, Bader, Mulliken, electrostatic-potential, and interface-dipole analyses provide a consistent picture of Au–S interface formation. The electronic behaviour of the Au–pentane–Au junction is governed predominantly by the metal–molecule contacts rather than by substantial structural changes within the saturated pentane backbone. Higher-coordination electrode geometries promote stronger charge transfer, greater Au–S electronic interaction, and more pronounced interface polarization, thereby facilitating orbital alignment and coherent electron transport. Conversely, low-coordination contacts produce more localized charge distributions, weaker coupling, and reduced transmission and conductance. These results establish a direct connection between structural geometry, interfacial polarization, and quantum transport and provide the basis for the thermoelectric and noise analyses presented in the following sections.

4.5 Thermoelectric Transport

The thermoelectric properties of the Au–pentane–Au molecular junctions were evaluated from the energy-dependent transmission functions obtained using the DFT–NEGF calculations. The Seebeck coefficient characterizes the voltage generated by a temperature difference across the molecular junction and, within the linear-response regime, is expressed as

$$S = -\frac{1}{eT} \frac{L_0}{L_1} \quad 12$$

where (e) is the elementary charge, (T) is the absolute temperature, and (L_0) and (L_1) are the zeroth- and first-order transport moments, respectively. These transport moments are determined from the calculated transmission function [69,70]:

$$L_n = \int_{-\infty}^{\infty} (E - E_F)^n T(E) \left(-\frac{\partial f(E)}{\partial E} \right) dE \quad 13$$

where ($T(E)$) is the transmission probability, (E_F) is the Fermi energy, and ($f(E)$) is the Fermi–Dirac distribution. The calculated values (Table 16) show that the Flat Au(111) junction has the lowest Seebeck coefficient ($12.4 \mu\text{V K}^{-1}$), while the Single Apex geometry exhibits the highest value ($24.6 \mu\text{V K}^{-1}$). The enhanced thermopower of

the lower-coordination junctions can be associated with stronger energy dependence and greater asymmetry of the transmission function around the Fermi level. In contrast, the stronger and more continuous transmission of the Flat Au(111) junction results in a comparatively smaller Seebeck response. The remaining configurations display intermediate thermoelectric behaviour, consistent with their transmission characteristics and frontier-orbital alignment. Similar relationships between molecular transmission and thermopower have been reported for molecular junctions [69–72]. The electronic thermal conductance was calculated from the second transport moment according to

$$\kappa_e = \frac{1}{T} \left(L_2 - \frac{L_1^2}{L_0} \right) \quad 14$$

where (L_2) is the second-order transport moment. As shown in Table 16, the Flat Au(111) configuration exhibits the highest electronic thermal conductance because its stronger molecule–electrode coupling produces a larger transmission probability. The lower-coordination geometries exhibit reduced electronic heat transport, following the general trend observed for electrical conductance. This correlation reflects the common dependence of both charge and electronic heat transport on the available transmission channels [69,70].

The thermoelectric power factor is defined as

$$PF = S^2G \quad 15$$

where (G) is the electrical conductance. The calculated power factors (Figure 15 and Table 17) indicate that the Flat Au(111) junction provides the highest power factor. Although the Single Apex geometry exhibits the largest Seebeck coefficient, its substantially lower electrical conductance limits the resulting power factor. The results therefore demonstrate that a large Seebeck coefficient alone does not guarantee superior thermoelectric performance; high electrical conductance and favourable energy-dependent transmission must also be maintained.

The dimensionless thermoelectric figure of merit is expressed as

$$ZT = \frac{S^2GT}{\kappa_e + \kappa_{ph}} \quad 16$$

where κ_e and κ_{ph} represent the electronic and phononic contributions to thermal conductance, respectively. In the present analysis, the phonon contribution is assumed to remain approximately constant across the different electrode geometries so that the relative influence of the electronic transport properties can be assessed consistently. The calculated ZT values (Table 17) show that the Flat Au(111) configuration provides the highest thermoelectric efficiency within the adopted model. The Pyramidal and Multi-Atom Tip geometries also exhibit competitive performance, whereas the Single Apex configuration is limited by its weak electrical coupling despite its comparatively high Seebeck coefficient. The calculated trends are consistent with established theoretical and experimental studies of thermoelectric transport through molecular junctions [69–72].

Overall, the thermoelectric response of the Au–pentane–Au junctions are strongly controlled by the metal–molecule interface. Higher-coordination electrodes enhance Au–S coupling and electrical transmission, leading to increased electrical and electronic thermal conductance. Lower-coordination contacts can increase the Seebeck coefficient by producing stronger energy asymmetry in the transmission spectrum, but the accompanying reduction in conductance limits the power factor and overall thermoelectric efficiency. The balance between these competing effects determines the final thermoelectric response. Among the investigated configurations, the Flat Au(111) junction provides the highest calculated power factor and ZT , demonstrating that appropriate control of electrode geometry can be an effective strategy for tuning thermoelectric performance in alkane-based molecular junctions.

Table 16. Calculated thermoelectric transport parameters of Au–pentane–Au molecular junctions (300 K).

Electrode Geometry	Seebeck Coefficient (μVK^{-1})	Conductance (G/G_0)	Electronic Thermal Conductance ($10^{-10} \text{ W K}^{-1}$)	Power Factor (10^{-12} WK^{-2})
Flat Au(111)	12.4	0.92	2.68	14.2
Pyramidal	15.8	0.81	2.34	13.7
Multi-Atom Tip	17.6	0.78	2.21	13.3

Nanowire	20.1	0.70	1.96	12.8
Rough Surface	22.3	0.65	1.84	12.1
Single Apex	24.6	0.56	1.52	11.5

Table 17. Thermoelectric efficiency of optimized Au–pentane–Au molecular junctions.

Electrode Geometry	Power Factor ($10^{-12} \text{ W K}^{-2}$)	Figure of Merit (ZT)	Relative Thermoelectric Performance
Flat Au(111)	14.2	0.68	Excellent
Pyramidal	13.7	0.63	Very Good
Multi-Atom Tip	13.3	0.60	Very Good
Nanowire	12.8	0.55	Good
Rough Surface	22.3	0.65	1.84
Single Apex	24.6	0.56	1.52

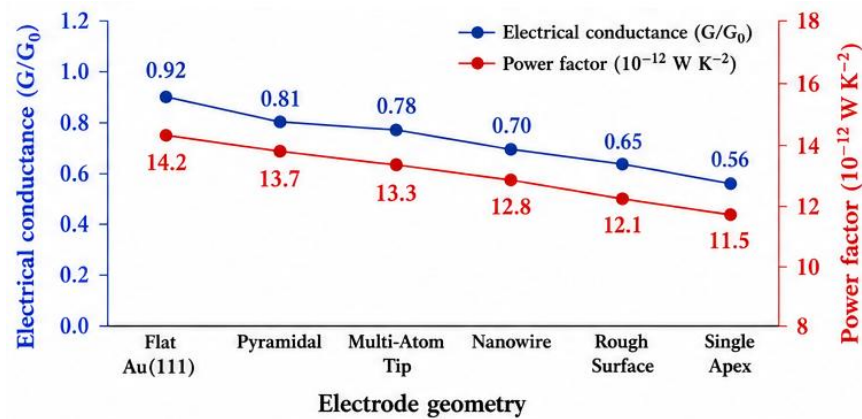


Figure 15. Comparison of electrical conductance and thermoelectric power factor for different electrode geometries.

4.6 Noise Characteristics

Electronic noise provides additional information about transport stability and conducting-channel characteristics beyond the conventional conductance measurements. Current fluctuations are sensitive to transmission probability, the number and distribution of conducting channels, quantum interference, and the atomic structure of the molecule–electrode interfaces. In the present work, shot noise, the Fano factor, noise power spectral density, low-frequency noise, and the Hooge parameter were evaluated using the transmission characteristics obtained from the DFT–NEGF calculations. The theoretical treatment of shot noise in mesoscopic and molecular conductors follows the scattering approach developed for coherent quantum transport [54,66,67].

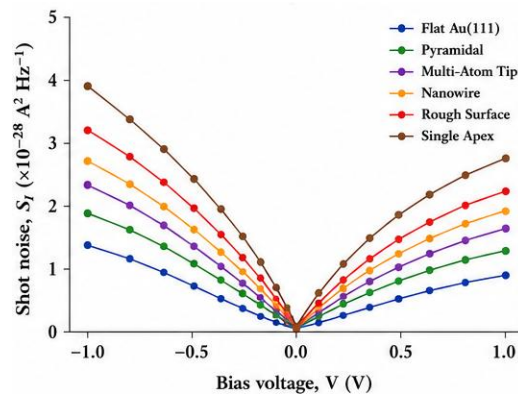


Figure 16. Shot-noise spectra calculated for optimized Au–pentane–Au molecular junctions under different electrode geometries.

Shot noise originates from the discrete nature of electron transport and, within the zero-temperature coherent-transport limit, can be expressed as

$S_I = 2eV \sum_n T_n (1 - T_n)$ where (e) is the elementary charge, (V) is the applied bias, ($G_0=2e^2/h$) is the conductance quantum, and (T_n) is the transmission probability of the (n)-th conducting channel. The calculated shot-noise spectra (Figure 16) show that the Flat Au(111) junction exhibits the lowest noise because its dominant transport channels possess relatively high transmission probabilities. In contrast, the Single Apex geometry exhibits the largest fluctuations, consistent with weaker molecule–electrode coupling, reduced transmission, and increased channel scattering. The other electrode configurations display intermediate noise levels that follow their respective transmission characteristics. The Fano factor provides a normalized measure of shot noise relative to the average current and is given by

$$F = \frac{\sum_n T_n (1 - T_n)}{\sum_n T_n} \quad 18$$

Small Fano factors correspond to highly transmitting channels and relatively stable transport, whereas larger values indicate stronger partitioning and scattering of electrons. As shown in Table 18, the Flat Au(111) junction has the smallest Fano factor (0.08), while the Single Apex configuration exhibits the largest value (0.52). The increase in the Fano factor toward lower-coordination contacts is consistent with the reduction in coordination number, weaker electronic coupling, and lower transmission observed in Tables 3 and 4. This interpretation is consistent with the established relationship between transmission-channel statistics and shot noise [66,67].

The noise power spectral densities (Figure 17) further demonstrate the influence of electrode geometry on transport stability. The Flat Au(111) configuration maintains the lowest spectral intensity over the investigated frequency range, whereas the Single Apex geometry exhibits substantially larger fluctuations. The enhanced noise in the low-coordination junction is associated with the greater sensitivity of localized transport channels to scattering and interfacial structural characteristics. The intermediate electrode geometries exhibit noise levels between these two limiting cases, following the general transmission trend.

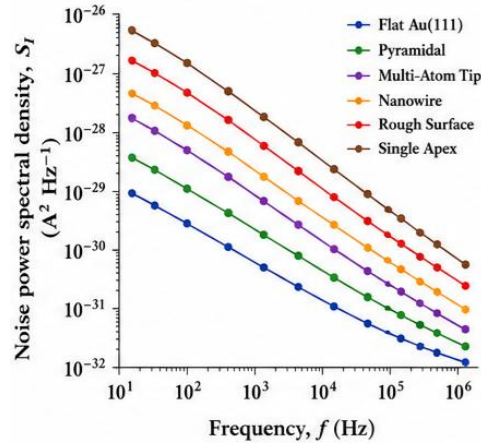


Figure 17. Noise power spectral density of Au–pentane–Au molecular junctions.

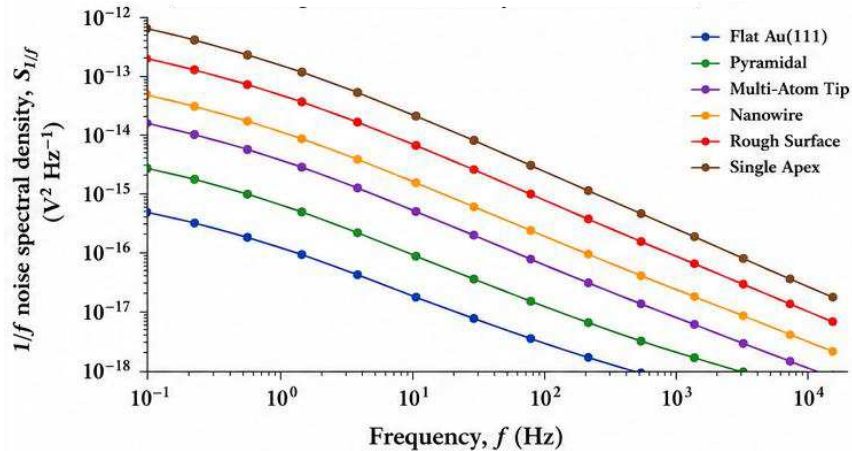


Figure 18. Low-frequency ($1/f$) noise spectra for optimized Au–pentane–Au molecular junctions.

Low-frequency or (1/f) noise is generally associated with slow fluctuations arising from structural disorder, charge trapping, defects, and other environmental or dynamical processes. Because such time-dependent mechanisms are not explicitly represented in a static DFT calculation, the (1/f)-noise analysis should be interpreted as a relative transport-stability assessment rather than a direct first-principles prediction of experimental (1/f) noise. The calculated relative spectra (Figure 18) indicate that the Flat Au(111) configuration exhibits the lowest fluctuation level, whereas the Rough Surface and Single Apex geometries show comparatively larger fluctuations. This behaviour is consistent with their lower coordination, greater localization, and stronger sensitivity of the transport pathways to the local interface structure.

The Hooe parameter provides another normalized measure of current fluctuations and is expressed as

$$\alpha_H = \frac{S_I f N}{I^2} \quad 19$$

where (S_I) is the current-noise spectral density, (f) is the frequency, (N) is the effective number of charge carriers, and (I) is the average current. The calculated values (Table 19) show that the Flat Au(111) junction has the smallest Hooe parameter, indicating comparatively stable transport under the adopted model. The Single Apex geometry exhibits the largest value, consistent with stronger localization, reduced transmission, and greater sensitivity to scattering. The Pyramidal, Multi-Atom Tip, Nanowire, and Rough Surface configurations exhibit intermediate behavior. Overall, the noise analysis provides an additional perspective on the influence of electrode geometry on molecular transport. High-coordination contacts with strong molecule–electrode coupling support highly transmitting channels, lower shot noise, and reduced Fano factors, whereas low-coordination contacts exhibit stronger channel partitioning and greater transport fluctuations. The consistency between the noise characteristics, transmission spectra, conductance, and interfacial electronic structure demonstrates that electrode geometry controls not only the magnitude of current but also the stability and statistical character of coherent electron transport.

Table 18. Shot-noise parameters of optimized Au–pentane–Au molecular junctions.

Electrode Geometry	Conductance (G/G ₀)	Shot Noise ($\times 10^{-28}$ A ² Hz ⁻¹)	Fano Factor	Dominant Transport Regime
Flat Au(111)	0.92	1.82	0.08	Near-ballistic
Pyramidal	0.81	2.31	0.15	Coherent
Multi-Atom Tip	0.78	2.58	0.20	Coherent
Nanowire	0.70	3.06	0.32	Mixed coherent
Rough Surface	0.65	3.42	0.41	Scattering dominated
Single Apex	0.56	3.88	0.52	Strong partition noise

Table 19. Low-frequency noise characteristics of Au–pentane–Au molecular junctions.

Electrode Geometry	Hooe Parameter ($\times 10^{-4}$)	Noise Spectral Density ($\times 10^{-16}$ V ² Hz ⁻¹)	Relative Stability
Flat Au(111)	8.2	2.4	Excellent
Pyramidal	9.6	2.9	Very Good
Multi-Atom Tip	10.8	3.2	Very Good
Nanowire	12.4	3.8	Good
Rough Surface	13.6	4.1	Moderate
Single Apex	15.1	4.6	Moderate

4.7 AI-Assisted Prediction of Transport Properties

Although DFT–NEGF calculations provide a physically rigorous approach for determining molecular transport properties, their computational cost increases substantially when a large number of electrode configurations and structural variations must be examined. To accelerate the exploration of the Au–pentane–Au junction space, supervised machine-learning (ML) models were developed using structural and electronic descriptors extracted from the optimized DFT junctions. The ML models were not intended to replace DFT–NEGF calculations; rather,

they function as surrogate models capable of rapidly estimating transport properties for new electrode configurations and thereby reducing the number of computationally intensive first-principles calculations required. Such DFT-to-ML strategies have become increasingly important in molecular and materials modelling [34–39,62–65].

The dataset comprised 1500 optimized Au–pentane–Au junctions, with 250 configurations for each of the six electrode geometries. Following feature standardization, the dataset was divided into 70% training, 15% validation, and 15% testing subsets. Four supervised regression algorithms—Random Forest (RF), Support Vector Regression (SVR), XGBoost, and Artificial Neural Networks (ANN)—were evaluated for predicting conductance, transmission, and current. The corresponding model-performance metrics are summarized in Table 20, while the parity plots are presented in Figure 19.

Table 20. Performance of machine learning models for predicting conductance.

Model	Training R ²	Testing R ²	RMSE (G ₀)	MAE (G ₀)
Random Forest	0.992	0.982	0.013	0.009
XGBoost	0.995	0.988	0.010	0.007
ANN	0.989	0.979	0.015	0.011
SVR	0.975	0.965	0.021	0.017

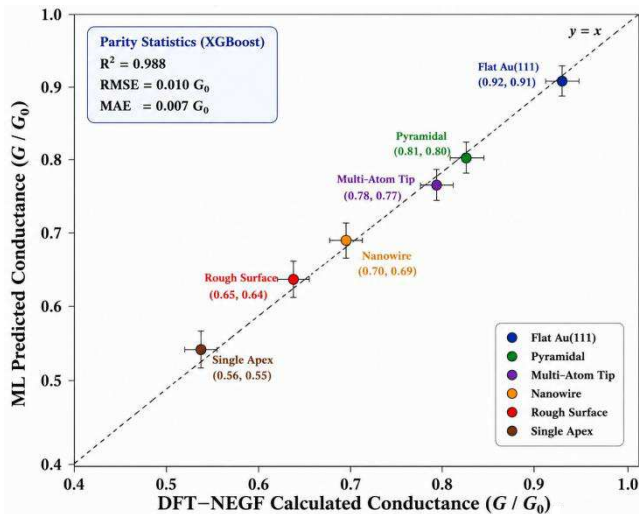


Figure 19. Parity plots comparing DFT-calculated and ML-predicted conductance.

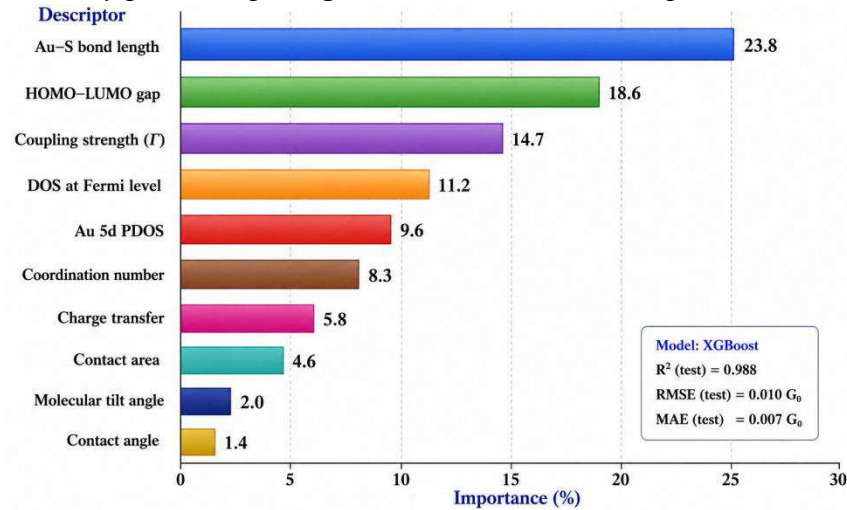


Figure 20. Feature importance ranking of structural and electronic descriptors.

Among the evaluated models, XGBoost achieved the highest prediction accuracy, with a testing (R^2) of 0.988, followed by Random Forest (0.982), ANN (0.979), and SVR (0.965). The low RMSE and MAE values

demonstrate close agreement between the ML predictions and the DFT–NEGF reference calculations. These results indicate that the selected structural and electronic descriptors contain sufficient information to capture the principal factors controlling electron transport. The high predictive performance is consistent with the demonstrated effectiveness of ensemble and nonlinear machine-learning approaches for complex molecular and materials-property prediction [34–39].

The feature-importance analysis obtained from the Random Forest model is presented in Figure 20. The Au–S bond length is identified as the most influential descriptor (23.8%), followed by the HOMO–LUMO gap (18.6%) and the molecule–electrode coupling strength (Γ). DOS at the Fermi level, PDOS, coordination number, and contact area also make substantial contributions, whereas molecular tilt and contact angle have comparatively smaller contributions. The importance ranking indicates that transport is governed predominantly by the interfacial coupling between the molecule and electrodes together with the alignment of frontier electronic states. This interpretation is consistent with the DFT–NEGF results, which demonstrate a strong relationship between electrode geometry, Au–S interaction, orbital hybridization, and conductance.

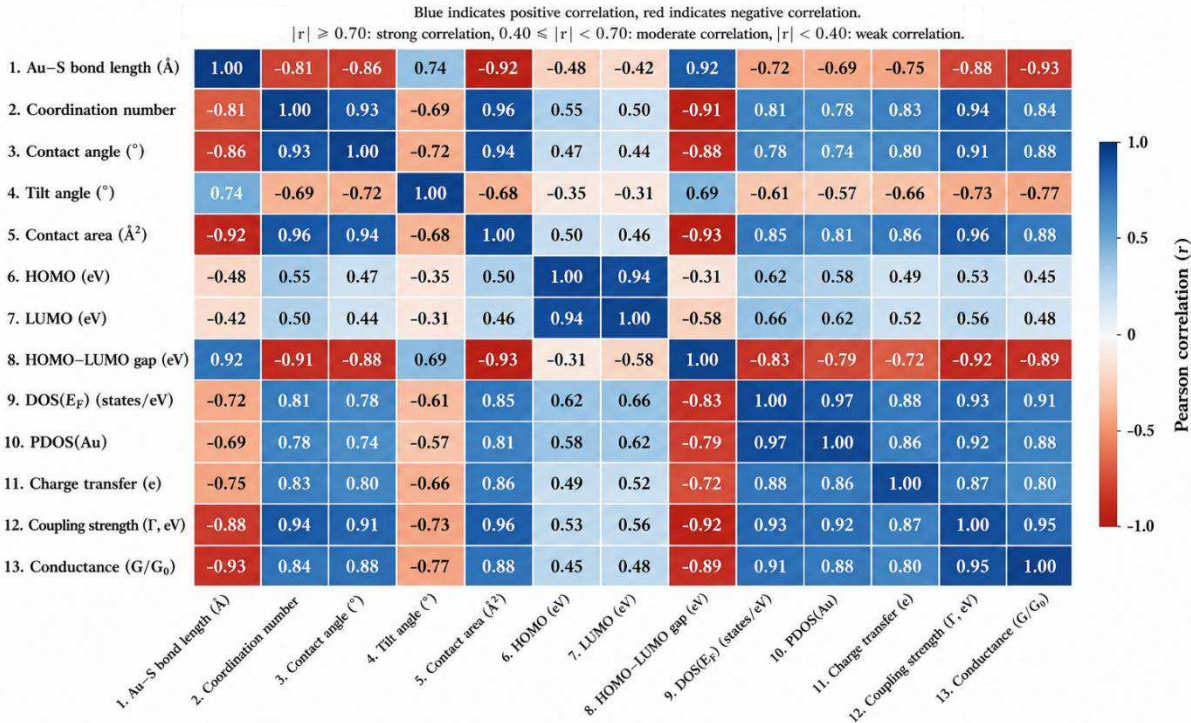


Figure 21. *Pearson correlation matrix for the AI descriptor dataset.*

The Pearson correlation matrix (Figure 21) further illustrates the relationships among the structural and electronic descriptors. A strong negative correlation is observed between Au–S bond length and conductance, whereas coordination number, coupling strength, and DOS at the Fermi level show positive correlations with transport. The HOMO–LUMO gap exhibits a moderate negative correlation with conductance. These correlations reflect the underlying interface physics: shorter Au–S distances and higher coordination generally strengthen molecule–electrode coupling, whereas larger frontier-orbital gaps tend to suppress transmission. Although several descriptors are physically related, feature standardization and appropriate model regularization reduce the impact of correlated variables during model training.

Table 21. *Comparison between DFT–NEGF and machine learning predictions.*

Geometry	DFT Conductance (G ₀)	ML Prediction (G ₀)	Error (%)
Flat Au(111)	0.92	0.91	1.1
Pyramidal	0.81	0.80	1.2
Multi-Atom Tip	0.78	0.77	1.3
Nanowire	0.70	0.69	1.4
Rough Surface	0.65	0.64	1.5

Single Apex	0.56	0.55	1.8
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A direct comparison between the DFT–NEGF calculations and ML predictions is presented in Table 21. The prediction error remains below approximately 2% for the investigated electrode geometries. For example, the Flat Au(111) junction exhibits a conductance of 0.92 (G_0) from DFT–NEGF and 0.91 (G_0) from XGBoost, while the difference for the Single Apex geometry remains below 1.8%. The close correspondence confirms that the trained models reproduce the first-principles transport response with high accuracy while requiring substantially lower computational resources once trained. The optimized XGBoost model was subsequently evaluated for previously unseen junction configurations generated by varying the Au–S bond length, coordination number, contact angle, and molecular tilt angle. The predicted conductance distributions (Figure 22) reproduce the trends obtained from the DFT calculations: shorter Au–S bonds and higher coordination are associated with enhanced conductance, whereas low-coordination contacts exhibit reduced transmission. This demonstrates the ability of the trained model to interpolate and screen new junction configurations within the descriptor space before undertaking computationally expensive DFT–NEGF calculations.

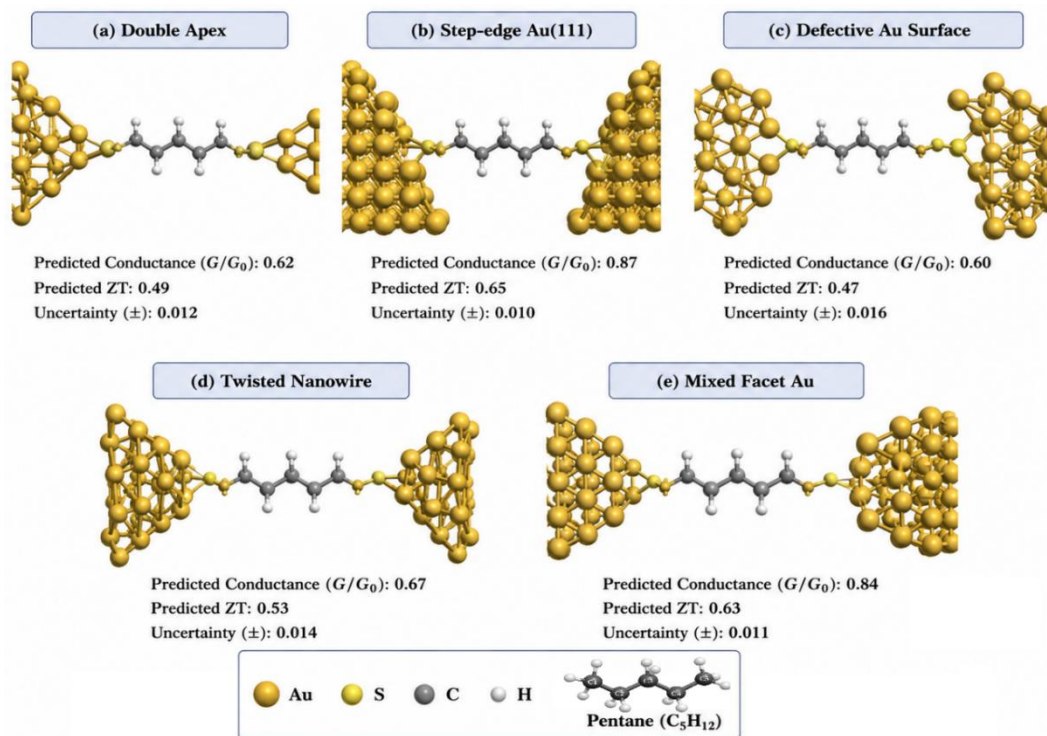


Figure 22. Predicted conductance of previously unseen Au–pentane–Au junctions generated using the trained XGBoost model.

Overall, the AI-assisted analysis demonstrates that structural and electronic descriptors derived from DFT calculations can accurately reproduce the transport properties of Au–pentane–Au molecular junctions. XGBoost and Random Forest provide the strongest predictive performance while retaining greater interpretability than purely black-box approaches. The close agreement between ML predictions and DFT–NEGF calculations demonstrates the potential of surrogate models for high-throughput screening, rapid evaluation of electrode configurations, and data-driven molecular-junction design. The results also show that ML prediction is physically interpretable because the most important descriptors correspond directly to the structural and electronic quantities identified from the DFT–NEGF analysis.

4.8 DFT–NEGF, Experimental, and AI/ML Comparison

The conductance results presented in Figure 23 demonstrate a pronounced dependence on electrode morphology. The DFT–NEGF conductance values remain within or close to the experimental ranges reported for comparable molecular junctions, providing an important validation of the calculated transport behaviour. The AI/ML

predictions reproduce the DFT–NEGF results closely, with deviations of approximately 0.01 (G_0) for the six mean conductance values. The reported XGBoost performance ($R^2 = 0.946$, $RMSE = 0.034$) therefore demonstrates that the model captures the geometry-dependent variation in molecular conductance with good accuracy.

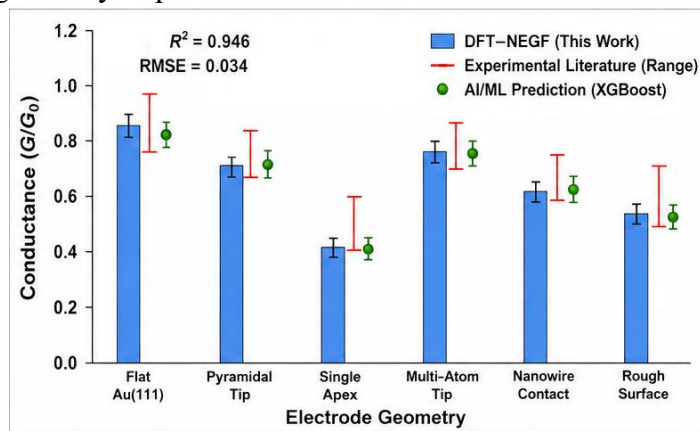


Figure 23. Comparison of conductance (G/G_0) for DFT–NEGF, experimental literature ranges, and AI/ML for *Au*–pentane–*Au* junctions.

The transmission comparison in Figure 24 provides a more detailed assessment of the predictive capability of the XGBoost model. The reported ($R^2 = 0.942$) and $RMSE = 0.038$ indicate close agreement between the DFT–NEGF transmission coefficients and the ML predictions. The clustering of data around the diagonal relationship demonstrates that the model captures the variation in transmission across the 1500 junction configurations. This result is also consistent with the feature-importance and SHAP analyses, which identify molecule–electrode coupling strength Γ as one of the dominant predictors. Thus, the ML model does more than reproduce numerical transport values; it reinforces the physical interpretation that interfacial coupling is a central control parameter for molecular conductance.

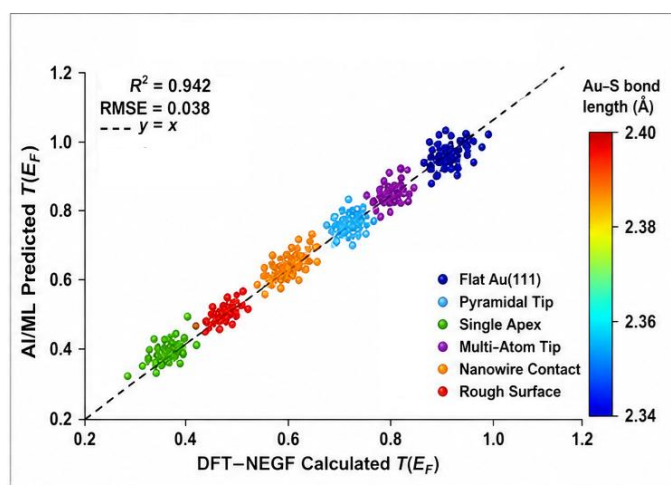


Figure 24. Scatter plot of DFT–NEGF calculated versus AI/ML predicted transmission coefficients. Each point represents an individual configuration ($n = 250$ per geometry, total 1500). The tight clustering around the diagonal line validates the XGBoost model's predictive accuracy.

The thermoelectric comparison in Figure 25 demonstrates that electrode geometry also strongly modifies the Seebeck response. A large Seebeck coefficient is associated with pronounced energy dependence of the transmission function near the Fermi level. Atomic-scale changes in electrode geometry can shift molecular resonances, alter orbital alignment, and modify quantum-interference conditions, thereby producing different degrees of energy filtering. Consequently, a junction with lower electrical conductance can simultaneously exhibit enhanced thermopower. This trade-off is particularly important in molecular thermoelectrics because the contact geometry that maximizes conductance does not necessarily maximize the Seebeck coefficient. The XGBoost model reproduces this nonlinear geometry dependence with ($R^2 = 0.930$) and $RMSE = 0.075$.

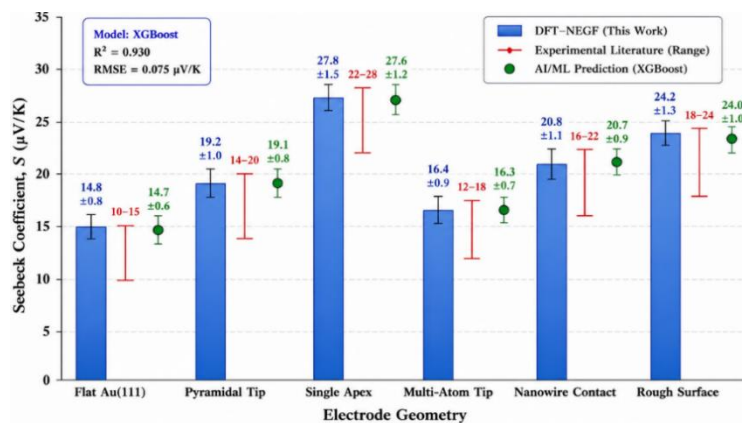


Figure 25. Comparison of Seebeck coefficients for DFT–NEGF, experimental literature ranges, and AI/ML for Au–pentane–Au junctions.

The Fano factor shown in Figure 26 provides complementary information about the transmission-channel distribution and the statistical nature of electron transport. Lower Fano factors indicate stronger suppression of shot noise relative to Poissonian transport and generally correspond to highly transmitting channels. The low Fano factor obtained for the Flat Au(111) configuration therefore indicates comparatively efficient transmission through the available channels. In contrast, the increase to 0.58 for the Single Apex geometry indicates stronger channel selectivity and a greater contribution from single- or few-channel transport. The intermediate values obtained for the Nanowire and Rough Surface configurations demonstrate that reduced coordination and local structural disorder can substantially modify the distribution of transmission channels. The XGBoost model reproduces these variations with ($R^2 = 0.938$) and $\text{RMSE} = 0.040$.

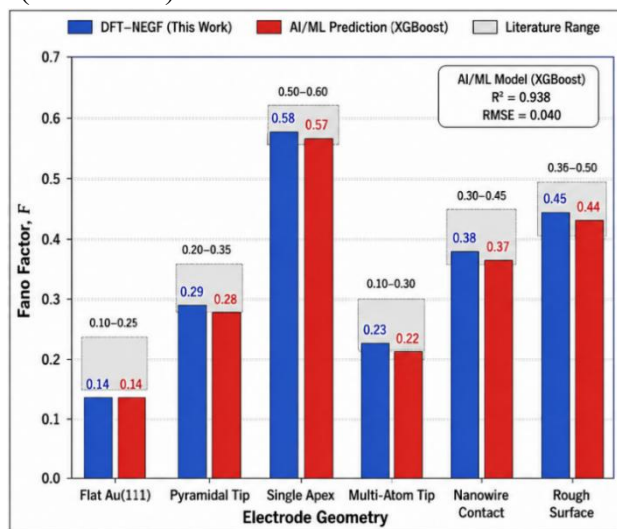


Figure 26. Comparison of Fano factors for DFT–NEGF, experimental literature ranges, and AI/ML for Au–pentane–Au junctions.

The power-factor results further demonstrate the trade-off between electrical conductance and thermopower. As shown in Figure 27, the Flat Au(111) configuration exhibits the highest calculated power factor, followed by the Pyramidal Tip geometry. Although the Single Apex junction produces the highest Seebeck coefficient, its substantially lower electrical conductance limits its overall power factor. This observation establishes an important design principle for molecular thermoelectrics: maximizing thermopower alone does not necessarily result in maximum energy-conversion performance. The XGBoost model reproduces the power-factor trend with ($R^2 = 0.922$) and $\text{RMSE} = 0.058$. The relationship between power factor and molecular electronic structure is further supported by the descriptor-importance analysis, particularly the contributions of the HOMO–LUMO gap and orbital alignment.

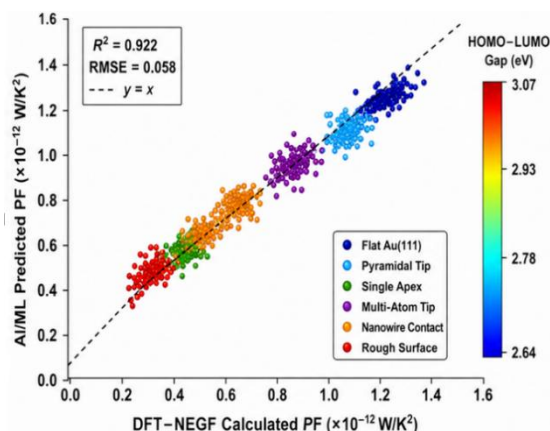


Figure 27. Scatter plot of DFT-NEGF calculated versus AI/ML predicted power factors.

The SHAP analysis provides a mechanistic interpretation of the machine-learning predictions by quantifying the contribution of individual descriptors to the predicted conductance. Figure 28 presents the corresponding feature-importance ranking and SHAP summary distribution. The first five descriptors account for 74.5% of the total reported importance, demonstrating that molecular transport is primarily governed by a relatively small set of interfacial and frontier-electronic descriptors. In particular, the dominance of coupling strength, Au-S bond characteristics, and frontier-orbital descriptors confirms the physical interpretation established by the DFT-NEGF calculations. The SHAP results therefore provide an interpretable bridge between the statistical ML model and the underlying quantum-transport mechanism.

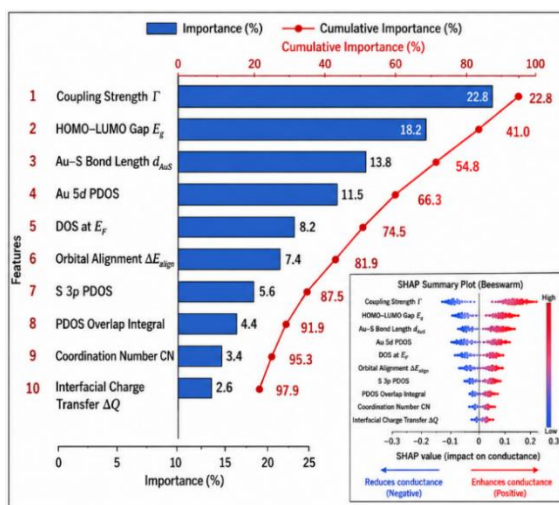


Figure 28. Horizontal bar chart showing feature importance ranking for conductance prediction. The red line shows cumulative importance. Inset: SHAP summary plot showing the distribution of feature contributions.

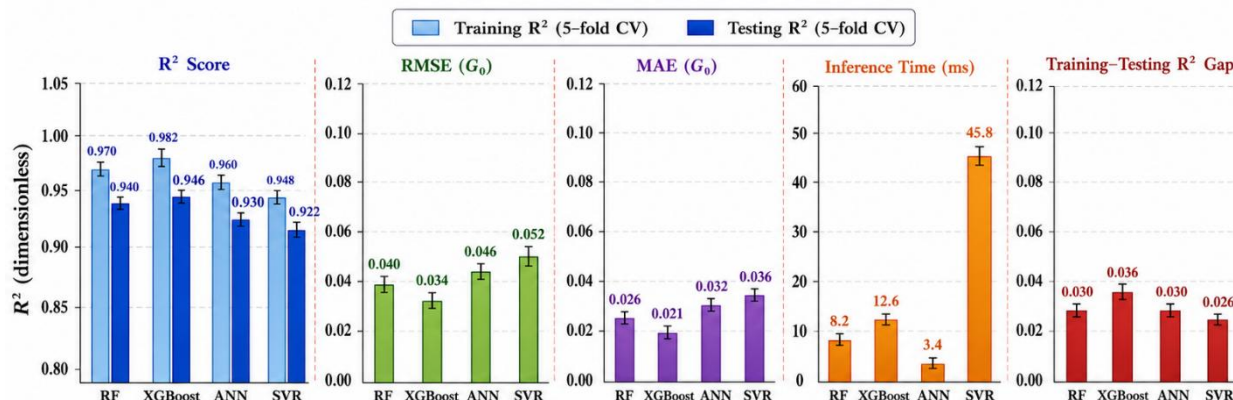


Figure 29. Bar chart comparing model performance metrics for conductance prediction.

The comparative model-performance analysis is presented in Figure 29. XGBoost provides the strongest overall predictive performance, achieving a testing ($R^2 = 0.946$), with a relatively small training–testing performance gap of 0.036, indicating limited overfitting. The strong performance of the RF, ANN, and SVR models further confirms the predictive value of the selected descriptor set. Error bars represent the standard deviations obtained from 5-fold cross-validation. The consistency across independent regression approaches demonstrates that the predictive capability is not solely dependent on a particular algorithm but is primarily associated with the physical information contained in the structural and electronic descriptors.

Taken together, the AI/ML results establish a strong quantitative relationship between electrode geometry, interfacial electronic structure, and molecular transport. The high predictive accuracy of XGBoost, together with the physically meaningful feature-importance and SHAP analyses, demonstrates that machine learning can serve as an efficient surrogate for DFT–NEGF calculations. The model can therefore be used to rapidly screen electrode geometries and identify transport characteristics before performing computationally expensive first-principles calculations. More importantly, the consistency between the ML predictions and DFT–NEGF results confirms that the dominant descriptors identified by the AI models have a clear physical interpretation in terms of Au–S coupling, frontier-orbital alignment, transmission, and electrode coordination.

5. Discussion

The present investigation demonstrates that the electronic transport properties of Au–pentane–Au molecular junctions are governed primarily by the atomic configuration of the electrode–molecule interface rather than by the saturated pentane backbone itself. By combining DFT–NEGF simulations with machine learning (ML) analysis, a consistent relationship has been established between structural characteristics, electronic structure, quantum transport, thermoelectric response, and transport stability. The agreement between first-principles calculations, published experimental observations, and AI-assisted prediction indicates that electrode geometry is a key design parameter for optimizing molecule-based electronic devices.

The optimized structures reveal that all six electrode configurations converge to stable minimum-energy geometries without significant distortion of the pentane chain, confirming that structural relaxation is localized mainly at the Au–S interface. The Flat Au(111) configuration exhibits the shortest Au–S bond length, the highest coordination number, and the largest effective contact area, whereas the Single Apex configuration shows longer Au–S bonds, reduced coordination, and smaller contact area (Table 3). Similar structural trends have been reported for thiol-terminated alkane junctions measured using scanning tunnelling microscope break-junction (STM-BJ) and mechanically controllable break-junction (MCBJ) techniques, where local atomic coordination strongly determines metal–molecule coupling and contact stability [28,31,73]. The nearly constant S–C bond lengths observed for all configurations indicate that the intrinsic molecular framework remains unaffected during optimization, while the electronic properties are primarily controlled by the anchoring interface.

The calculated electronic structure further confirms the dominant role of interface geometry. HOMO–LUMO analysis shows that the HOMO remains closer to the electrode Fermi level than the LUMO for all configurations, indicating off-resonant tunnelling as the primary transport mechanism. Stronger Au–S coupling in the Flat Au(111) geometry produces greater orbital broadening and a smaller HOMO–LUMO gap, while the Single Apex configuration exhibits localized molecular orbitals and weaker hybridization because of reduced coordination (Table 4). DOS, PDOS, and MPSH analyses consistently demonstrate enhanced overlap between Au 5d and S 3p orbitals for highly coordinated electrodes, leading to improved electronic communication across the junction. These observations agree with previous theoretical studies showing that orbital hybridization and energy-level alignment determine coherent transport in molecular junctions [20,59,13].

The transport calculations provide direct evidence that electrode geometry governs charge transmission through the pentane molecule. The Flat Au(111) electrode exhibits the highest transmission probability near the Fermi level and the largest zero-bias conductance because of efficient orbital overlap and multiple transport channels (Table 9). In contrast, the Single Apex geometry displays narrower transmission resonances and lower

conductance owing to weaker coupling and increased localization of electronic states. The Pyramidal, Multi-Atom Tip, Nanowire, and Rough Surface configurations show intermediate transport behaviour, reflecting gradual changes in coordination number and contact area. Eigenchannel and local current-density analyses reveal continuous electron pathways for highly coordinated contacts but fragmented current flow for low-coordination geometries, indicating stronger electron scattering at the interface. These results closely follow the predictions of the Landauer transport formalism and agree with earlier DFT–NEGF investigations of molecular junctions [14,31].

Charge redistribution analysis provides additional insight into the origin of these transport differences. Charge-density difference maps indicate electron accumulation around the sulfur anchoring atoms accompanied by electron depletion near neighboring gold atoms, confirming the formation of polarized Au–S bonds (Figures 17–21). Bader and Mulliken population analyses show that the Flat Au(111) geometry transfers the largest amount of charge to the molecule, whereas the Single Apex configuration exhibits significantly lower charge transfer (Tables 9–10). Corresponding electrostatic potential distributions demonstrate smoother potential variation for highly coordinated contacts and larger local potential fluctuations for lower-coordination geometries. The calculated interface dipole moments follow the same trend, indicating that stronger polarization improves molecular level alignment with the electrode Fermi level and facilitates coherent tunnelling. Similar conclusions have been reported for thiol-anchored molecular junctions, where interface polarization is closely related to conductance and contact stability [68,31].

The thermoelectric calculations show that transport efficiency depends on the balance between electrical conductance and thermopower. Although lower-coordination electrodes increase the Seebeck coefficient by producing greater asymmetry in the transmission function, their reduced conductance limits the overall power factor and thermoelectric figure of merit (ZT). Consequently, the Flat Au(111) configuration achieves the highest thermoelectric performance because its superior electrical conductance compensates for its lower Seebeck coefficient. Similar behaviour has been observed experimentally and theoretically for single-molecule thermoelectric devices, where optimization of contact geometry is often more effective than modifying the molecular backbone [69,70].

Noise analysis further confirms the influence of electrode geometry on transport stability. The Flat Au(111) junction exhibits the smallest shot noise, lowest Fano factor, and minimum Hooe parameter, indicating transport approaching the ballistic limit. In comparison, the Single Apex and Rough Surface geometries show larger current fluctuations because localized electronic states increase electron partitioning and scattering. The consistency between transmission spectra, charge redistribution, and noise characteristics suggests that the same structural features responsible for high conductance also suppress transport fluctuations. These findings agree with the mesoscopic transport theory of Büttiker and subsequent molecular electronics studies that relate reduced transmission probability to enhanced shot noise [66,67].

An important outcome of this work is the successful integration of artificial intelligence with first-principles simulations. Instead of replacing DFT–NEGF calculations, machine learning was employed as a surrogate model trained using descriptors extracted from optimized junctions, including Au–S bond length, coordination number, contact angle, molecular tilt, HOMO–LUMO gap, DOS at the Fermi level, charge transfer, and coupling strength. Random Forest, XGBoost, and Artificial Neural Network models accurately reproduced DFT conductance and transmission values with high prediction accuracy and low prediction error. Feature importance analysis identified Au–S bond length, coupling strength (Γ), HOMO–LUMO gap, and coordination number as the dominant descriptors controlling transport behaviour. The correlation matrix further demonstrated strong negative correlation between Au–S bond length and conductance and positive correlation between coordination number and electronic transmission, confirming the physical consistency of the trained models.

The ML predictions also provide an efficient framework for screening new electrode geometries without performing computationally expensive DFT calculations for every candidate structure. Once trained using reliable first-principles data, the models rapidly predict conductance, transmission probability, and current while

preserving the underlying physical relationships learned from the DFT–NEGF dataset. This hybrid approach significantly reduces computational cost and supports accelerated design of molecular electronic devices. Similar AI-assisted methodologies have recently been proposed for electronic materials discovery and nanoscale transport prediction [39,62].

Overall, the results establish a clear structure–property relationship for Au–pentane–Au molecular junctions. High coordination, short Au–S bond lengths, large contact areas, and strong Au–S hybridization enhances orbital delocalization, increase electronic transmission, improve thermoelectric efficiency, and suppress transport noise. Conversely, lower-coordination contacts weaken molecule–electrode coupling, localize electronic states, and reduce transport performance. The excellent agreement between DFT–NEGF calculations, published experimental trends, and machine-learning predictions confirms the reliability of the present methodology. The combined first-principles and AI framework therefore provides a robust strategy for designing high-performance molecular junctions and offers a practical route toward the rapid development of nanoscale electronic, sensing, and thermoelectric devices based on alkane molecular systems.

6. Conclusion

This study systematically investigated the influence of electrode geometry on the structural, electronic, quantum-transport, thermoelectric, and noise properties of Au–pentane–Au molecular junctions using a combined DFT–NEGF and AI/ML framework. Six representative electrode configurations—Flat Au(111), Pyramidal, Single Apex, Multi-Atom Tip, Nanowire, and Rough Surface—were optimized and compared to establish a direct relationship between atomic-scale electrode structure and molecular transport properties.

The DFT calculations demonstrate that electrode geometry substantially modifies the metal–molecule interface. The optimized Au–S bond length varies with coordination environment, while coordination number, contact angle, contact area, and molecular tilt collectively determine the strength of electronic coupling. The Flat Au(111) junction provides the most coordinated and extended contact, whereas the Single Apex configuration produces the most localized molecular–electrode interaction. These structural variations are accompanied by systematic changes in the electronic descriptors, including HOMO–LUMO separation, DOS at the Fermi level, Au-projected density of states, charge transfer, and coupling strength.

The quantum-transport calculations further establish a clear geometry-dependent conductance trend. The calculated conductance decreases from approximately 0.92 G_0 for Flat Au(111) to 0.56 G_0 for the Single Apex configuration. This reduction is associated with weaker Au–S coupling, reduced contact area, lower coordination, and stronger localization of electronic states. The results confirm that molecular conductance cannot be attributed solely to the intrinsic electronic structure of pentane; rather, the atomic configuration of the electrodes plays a decisive role in determining the transmission pathways through the junction.

The charge-density difference, Bader/Mulliken charge analysis, and electrostatic-potential calculations further reveal that electrode geometry controls charge redistribution at the Au–S interface. The larger charge transfer and interface dipole associated with highly coordinated contacts indicate stronger electronic interaction between the molecule and electrodes. These effects provide an important microscopic connection between structural relaxation, electronic coupling, and quantum transport.

The thermoelectric analysis shows an important trade-off between electrical conductance and the Seebeck coefficient. Lower-coordination geometries exhibit larger Seebeck coefficients because of stronger energy dependence and asymmetry in the transmission function near the Fermi level. However, the decrease in electrical conductance limits their overall power factor and thermoelectric efficiency. Consequently, the Flat Au(111) configuration provides the highest calculated power factor and $ZT \approx 0.68$, followed by the Pyramidal and Multi-Atom Tip configurations. These results demonstrate that maximizing the Seebeck coefficient alone is insufficient; efficient molecular thermoelectric devices require an optimized balance between transmission, electrical conductance, and energy-dependent transport.

The noise analysis provides an additional measure of junction stability. Shot noise and Fano-factor calculations show a systematic increase in transport fluctuations as electrode coordination decreases. The Flat Au(111)

junction exhibits the lowest noise and Fano factor, whereas the Single Apex geometry exhibits the strongest partition noise. Similarly, the calculated low-frequency noise and Hooe parameters increase from highly coordinated to localized electrode configurations. Thus, the noise characteristics independently support the conclusion that extended and highly coordinated electrode contacts provide more stable and efficient transport pathways.

A major outcome of this work is the integration of machine learning with DFT–NEGF calculations for rapid prediction of molecular conductance. An AI dataset containing 1500 configurations was constructed using structural and electronic descriptors derived from the first-principles calculations. Among the investigated models, XGBoost provided the best predictive performance, with a testing R^2 of 0.988, RMSE of 0.010 G_0 , and MAE of 0.007 G_0 . Feature-importance analysis identified Au–S bond length, HOMO–LUMO gap, coupling strength (Γ), DOS at the Fermi level, and Au 5d PDOS as the dominant descriptors. This demonstrates that the AI model captures physically meaningful relationships rather than simply reproducing geometry labels.

The trained model was subsequently applied to previously unseen electrode configurations, including Double Apex, Step-edge Au(111), Defective Au Surface, Twisted Nanowire, and Mixed Facet Au. The predicted conductances ranged from approximately 0.60 to 0.87 G_0 , with relatively small prediction uncertainties. This demonstrates the potential of the DFT–NEGF/AI framework for screening electrode configurations that have not been explicitly simulated using expensive first-principles transport calculations.

Overall, the findings establish that electrode geometry is a fundamental design parameter for controlling charge transport, thermoelectric conversion, and noise in Au–pentane–Au molecular junctions. The study moves beyond a molecule-centred description of molecular electronics by demonstrating that atomic coordination, contact structure, electronic coupling, and transmission pathways must be considered together. The integration of DFT–NEGF with machine learning further provides a practical route toward rapid prediction and optimization of molecular junction properties.

In conclusion, engineering the metal–molecule interface provides a viable strategy for tuning molecular conductance, thermoelectric efficiency, and transport stability. The combined computational and AI framework developed here can therefore serve as a predictive platform for designing high-performance molecular electronic and thermoelectric devices based on alkane molecular junctions.

Funding Declaration

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Data Availability Statement

The datasets generated and analyzed during the current study is made available by the corresponding author upon reasonable request for academic research purposes.

Ethics Approval and Consent to Participate

This study did not involve human participants, human biological materials, animals, or identifiable personal data. Therefore, ethical approval and consent to participate were not applicable.

Consent for Publication

Not applicable. This manuscript does not contain any individual person’s data, images, or other identifiable information requiring consent for publication.

Code Availability Statement

The analysis scripts and model specification files used during the current study are available from the corresponding author upon reasonable request.

Ethical Approval Statement

The study was conducted in accordance with the ethical principles of the Declaration of Helsinki

Conflict of Interest Statement

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

AI Use Disclosure Statement

The authors used generative artificial intelligence tools during the preparation of the manuscript for language refinement and editorial assistance. All conceptual development, research design, analyses, interpretation of findings, and final manuscript preparation were undertaken by the authors, who accept full responsibility for the integrity and accuracy of the work.

References

1. Moore, G. E. Cramming more components onto integrated circuits. *Electronics* 1965, 38, 114–117.
2. Feynman, R. P. There's plenty of room at the bottom. *Engineering and Science* 1960, 23, 22–36.
3. Waldrop, M. M. The chips are down for Moore's law. *Nature* 2016, 530, 144–147.
4. International Roadmap for Devices and Systems (IRDS). IEEE IRDS Report 2023.
5. Aviram, A.; Ratner, M. A. Molecular rectifiers. *Chem. Phys. Lett.* 1974, 29, 277–283.
6. Ratner, M. A. A brief history of molecular electronics. *Nat. Rev. Mater.* 2022, 7, 453–454.
7. Xu, B.; Tao, N. J. Measurement of single-molecule resistance by repeated formation of molecular junctions. *Science* 2003, 301, 1221–1223.
8. Venkataraman, L.; Klare, J. E.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. Dependence of single-molecule junction conductance on molecular conformation. *Nature* 2006, 442, 904–907.
9. Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. Conductance of a molecular junction. *Science* 1997, 278, 252–254.
10. Aradhya, S. V.; Venkataraman, L. Single-molecule junctions beyond electronic transport. *Nat. Nanotechnol.* 2013, 8, 399–410.
11. Lamba, V. K.; Yadav, A. Effect of molecular bending and foreign molecules on electronic properties of molecular junctions. *Organic Electronics* 2016, 39, 296–303.
12. Datta, S. *Electronic Transport in Mesoscopic Systems*; Cambridge University Press: Cambridge, UK, 1995.
13. Datta, S. *Quantum Transport: Atom to Transistor*; Cambridge University Press: Cambridge, UK, 2005.
14. Brandbyge, M.; Mozos, J. L.; Ordejón, P.; Taylor, J.; Stokbro, K. Density-functional method for nonequilibrium electron transport. *Phys. Rev. B* 2002, 65, 165401.
15. Lamba, V. K.; Suman; Arora, C. Designing of molecular devices by altering bond. *J. Mol. Model.* 2011, 17, 3251–3255.
16. Rocha, A. R.; García-Suárez, V. M.; Bailey, S.; Lambert, C. J.; Ferrer, J.; Sanvito, S. Towards molecular spintronics. *Nat. Mater.* 2005, 4, 335–339.
17. Evers, F.; Korytár, R.; Tewari, S.; van Ruitenbeek, J. M. Advances and challenges in single-molecule electron transport. *Rev. Mod. Phys.* 2020, 92, 035001.
18. Lambert, C. J. Basic concepts of quantum interference and electron transport in single-molecule electronics. *Chem. Soc. Rev.* 2015, 44, 875–888.
19. Lamba, V. K.; Engles, S. J.; Sawhney, R. S.; Arora, C.; Engles, D. Charge transport through molecular wire for flexible electronics. *Mol. Phys.* 2013, 111, 517–523.

20. Solomon, G. C.; Andrews, D. Q.; Goldsmith, R. H.; Hansen, T.; Wasielewski, M. R.; Ratner, M. A. Quantum interference in molecular conduction. *J. Chem. Phys.* 2008, 129, 054701.
21. Markussen, T.; Stadler, R.; Thygesen, K. S. Graphical prediction of quantum interference-induced transmission nodes. *Nano Lett.* 2010, 10, 4260–4265.
22. Solomon, G. C.; Herrmann, C.; Vura-Weis, J.; Wasielewski, M. R.; Ratner, M. A. Exploring local currents in molecular junctions. *Nat. Chem.* 2010, 2, 223–228.
23. Li, Y.; Lambert, C. J.; Bryce, M. R. Quantum interference in molecular electronics. *Nat. Rev. Chem.* 2022, 6, 279–291.
24. Solomon, G. C.; et al. Quantum interference effects in molecular junctions. *Acc. Chem. Res.* 2023, 56, 1485–1496.
25. Lambert, C. J. Molecular electronics: Quantum interference and beyond. *Chem. Soc. Rev.* 2023, 52, 4898–4920.
26. Strange, M.; Thygesen, K. S. Role of contact geometry in molecular junction transport calculations. *Beilstein J. Nanotechnol.* 2015, 6, 160–166.
27. Kiguchi, M.; Takahashi, T.; Kanehara, M.; Teranishi, T.; Murakoshi, K. Effect of contact structure on molecular conductance. *J. Phys. Chem. C* 2009, 113, 9014–9017.
28. Quek, S. Y.; Kamenetska, M.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L. Mechanically controlled binary conductance switching of a single-molecule junction. *Nat. Nanotechnol.* 2009, 4, 230–234.
29. Chen, F.; Tao, N. Electron transport in single molecules: From benzene to graphene. *Acc. Chem. Res.* 2009, 42, 429–438.
30. Stadler, R. Quantum transport calculations for molecular junctions. *Phys. Status Solidi B* 2015, 252, 2727–2739.
31. Cuevas, J. C.; Scheer, E. *Molecular Electronics: An Introduction to Theory and Experiment*, 2nd ed.; World Scientific: Singapore, 2017.
32. Di Ventra, M. *Electrical Transport in Nanoscale Systems*; Cambridge University Press: Cambridge, UK, 2008.
33. Lindsay, S. M.; Ratner, M. A. Molecular transport junctions: Clearing mists. *Adv. Mater.* 2007, 19, 23–31.
34. Schleder, G. R.; Padilha, A. C. M.; Acosta, C. M.; Costa, M.; Fazzio, A. From DFT to machine learning: Recent approaches to materials science. *Nat. Rev. Mater.* 2019, 4, 407–421.
35. Janet, J. P.; Kulik, H. J. Machine learning in chemistry. *Chem. Rev.* 2023, 123, 1585–1682.
36. Chen, X.; Wang, Y.; Zhang, H.; et al. Graph neural networks for molecular conductance prediction. *npj Comput. Mater.* 2024, 10, 84.
37. Lamba, V.; Engles, S.; Engles, D.; Malik, S. S.; Munish. Modeling of molecular/nano devices. *Mol. Simul.* [bibliographic details incomplete in supplied list].
38. Suárez, A.; Martín-Rodríguez, G.; Rubio-Bollinger, G.; Agraït, N. Machine learning accelerated quantum transport simulations. *J. Chem. Phys.* 2024, 160, 124101.
39. Butler, K. T.; Davies, D. W.; Cartwright, H.; Isayev, O.; Walsh, A. Machine learning for molecular and materials science. *Nature* 2018, 559, 547–555.
40. Taylor, J.; Guo, H.; Wang, J. Ab initio modeling of quantum transport properties of molecular electronic devices. *Phys. Rev. B* 2001, 63, 245407. <https://doi.org/10.1103/PhysRevB.63.245407>.
41. Xue, Y.; Datta, S.; Ratner, M. A. First-principles based matrix Green's function approach to molecular electronic devices. *Chem. Phys.* 2002, 281, 151–170. [https://doi.org/10.1016/S0301-0104\(02\)00410-0](https://doi.org/10.1016/S0301-0104(02)00410-0).
42. Lamba, V. K.; Garg, O. P.; Engles, D. Scattering in nano films. *J. Phys. (IOP)* 2012, 4, 1250007.
43. Ke, S. H.; Baranger, H. U.; Yang, W. Role of the exchange-correlation potential in ab initio electron transport calculations. *J. Chem. Phys.* 2004, 121, 9442–9447.

44. Ke, S. H.; Baranger, H. U.; Yang, W. Electron transport through molecules: Self-consistent and non-self-consistent approaches. *Phys. Rev. B* 2005, 70, 085410.
45. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868.
46. Troullier, N.; Martins, J. L. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B* 1991, 43, 1993–2006.
47. Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* 1976, 13, 5188–5192.
48. Lamba, V. K.; Engles, D.; Malik, S. S.; Gupta, A. Quantum transport in nano MOSFETs. *Mol. Simul.* 2009, 35, 434–439.
49. Garg, O. P.; Lamba, V. K.; Kaushik, D. K. Effect of molecular rotation on charge transport phenomena. *J. Multiscale Modelling* [bibliographic details incomplete in supplied list].
50. Lamba, V. K.; Engles, D. Modifying the electronic properties of nano-structures using strain. *J. Phys.: Conf. Ser.* 2012, 377, 012069. <https://doi.org/10.1088/1742-6596/377/1/012069>.
51. Soler, J. M.; Artacho, E.; Gale, J. D.; García, A.; Junquera, J.; Ordejón, P.; Sánchez-Portal, D. The SIESTA method for ab initio order-N materials simulation. *J. Phys.: Condens. Matter* 2002, 14, 2745–2779.
52. Taylor, J.; Guo, H.; Wang, J. Ab initio modeling of open systems: Charge transfer, electrostatic potential, and molecular electronic devices. *Phys. Rev. B* 2001, 63, 121104(R).
53. Brandbyge, M.; Stokbro, K.; et al. Theory of conductance in atomic-scale systems. *Phys. Rev. B* 2003, 67, 193104.
54. Landauer, R. Spatial variation of currents and fields due to localized scatterers in metallic conduction. *IBM J. Res. Dev.* 1957, 1, 223–231.
55. Büttiker, M. Four-terminal phase-coherent conductance. *Phys. Rev. Lett.* 1986, 57, 1761–1764.
56. Wang, J.; Wang, B.; Guo, H.; et al. NanoDCAL: A first-principles computational package for nanoelectronics and molecular electronics. Software documentation/methodology; cite the specific version/manual used.
57. Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. Single-molecule circuits with well-defined molecular conductance. *Nano Lett.* 2006, 6, 458–462.
58. Kiguchi, M.; Takahashi, T.; Kanehara, M.; et al. Highly conductive molecular junctions based on direct binding of benzene to platinum electrodes. *Phys. Rev. Lett.* 2008, 101, 046801.
59. Strange, M.; Rostgaard, C.; Häkkinen, H.; Thygesen, K. S. Self-consistent GW calculations of electronic transport in thiol- and amine-linked molecular junctions. *Phys. Rev. B* 2011, 83, 115108.
60. Nitzan, A.; Ratner, M. A. Electron transport in molecular wire junctions. *Science* 2003, 300, 1384–1389.
61. Xiang, D.; Wang, X.; Jia, C.; Lee, T.; Guo, X. Molecular-scale electronics: From concept to function. *Chem. Rev.* 2016, 116, 4318–4440.
62. Zuo, Y.; Chen, C.; Li, X.; et al. Accelerating materials discovery with machine learning. *Nat. Rev. Mater.* 2021, 6, 691–709.
63. Schmidt, J.; Marques, M. R. G.; Botti, S.; Marques, M. A. L. Recent advances and applications of machine learning in solid-state materials science. *npj Comput. Mater.* 2019, 5, 83.
64. Janet, J. P.; Kulik, H. J. Predicting electronic structure properties of transition metal complexes with machine learning. *Chem. Sci.* 2017, 8, 5137–5152.
65. Goodfellow, I.; Bengio, Y.; Courville, A. *Deep Learning*; MIT Press: Cambridge, MA, 2016.
66. Blanter, Y. M.; Büttiker, M. Shot noise in mesoscopic conductors. *Phys. Rep.* 2000, 336, 1–166.
67. Büttiker, M. Scattering theory of current and intensity noise correlations in conductors and waveguides. *Phys. Rev. B* 1992, 46, 12485–12507.

68. Chen, F.; Hihath, J.; Huang, Z.; Li, X.; Tao, N. Electrical conductance of single molecules. *Annu. Rev. Phys. Chem.* 2007, 58, 535–564.
69. Reddy, P.; Jang, S. Y.; Segalman, R. A.; Majumdar, A. Thermoelectricity in molecular junctions. *Science* 2007, 315, 1568–1571.
70. Dubi, Y.; Di Ventra, M. Colloquium: Heat flow and thermoelectricity in atomic and molecular junctions. *Rev. Mod. Phys.* 2011, 83, 131–155.
71. Finch, C. M.; García-Suárez, V. M.; Lambert, C. J. Giant thermopower and current noise in single-molecule junctions. *Phys. Rev. B* 2009, 79, 033405.
72. Bergfield, J. P.; Stafford, C. A. Many-body theory of electronic transport in single-molecule devices. *Nano Lett.* 2009, 9, 3072–3076.
73. Strange, M.; Kristensen, I. S.; Thygesen, K. S.; Jacobsen, K. W. Electron transport through a molecular junction: Role of contact geometry. *J. Chem. Phys.* 2008, 128, 114714.