

## CHAPTER III

### COMPUTATIONAL DETAILS

In this thesis, we used density functional theory to describe the quantum behavior of atoms, molecules, and 2D materials. To study single atom (SA) and dual atom (DA) decoration on  $V_2CO_2$ , various computational methods were employed, providing understanding for suggestions of the most suitable surface as a cathode material for Al-S batteries. This chapter provides an overview of the theoretical and computational methods used in this thesis. It begins with an introduction to the fundamentals of the Schrödinger equation for multi-particle systems (Section 3.1), followed by a detailed explanation of the core principles of DFT (Section 3.2).

Subsequently, the methodology for structural optimization, a crucial step in providing stable structures, is described in Section 3.3. To address the errors inherent in DFT calculations, techniques for error correction are discussed in Section 3.4. For studying the reaction kinetics of  $Al_2S_3$  decomposition, the climbing image-nudged elastic band (CI-NEB) method is introduced in Section 3.5.

To further understand the sulfur reduction reaction (SRR) process with the bare and modified  $V_2CO_2$  surfaces, Gibbs free energy (G) calculations were employed, as detailed in Section 3.6. The Smooth Overlap of Atomic Positions (SOAP) is used to gain deeper insight into the correlation between structural changes, adsorption, and deformation energy in Section 3.7. The crystal orbital Hamilton population (COHP) method, used to evaluate bond strength, is described in Section 3.8. All these methodologies were summarized in Section 3.9.

### 3.1 Schrödinger equation for many particles

Understanding the quantum behavior of systems with multiple particles is fundamentally grounded in the Schrödinger equation. Formulated by Erwin Schrödinger in the 1920s, this equation provides a mathematical framework for describing the wavefunctions of complex systems. The general form of the Schrödinger equation can be written

$$\hat{H}\Psi(\vec{R}_i, \vec{r}_j) = E\Psi(\vec{R}_i, \vec{r}_j) \quad (3.1)$$

The equation is an eigenvalue equation where  $\hat{H}$  is the Hamiltonian operator,  $\Psi$  is the wavefunction dependent on the coordinates of nuclei ( $\vec{R}_i$ ) and electrons ( $\vec{r}_j$ ), and  $E$  is the energy eigenvalue of the system. The Hamiltonian operator consists of kinetic energy and potential energy terms for nuclei and electrons. Thus, the Hamiltonian can be written as

$$\begin{aligned} \hat{H} &= T_N + T_e + V_{NN} + V_{Ne} + V_{ee} \\ &= -\sum_{i=1}^N \frac{\hbar^2}{2M_i} \nabla_{R_i}^2 - \sum_{j=1}^n \frac{\hbar^2}{2m_j} \nabla_{r_j}^2 + \frac{1}{2} \sum_{i=1}^N \sum_{i'=1}^N \frac{1}{4\pi\epsilon_0} \frac{Z_i Z_{i'} e^2}{|R_i - R_{i'}|} \\ &\quad - \sum_{i=1}^N \sum_{j=1}^n \frac{1}{4\pi\epsilon_0} \frac{Z_i e^2}{|R_i - r_j|} + \frac{1}{2} \sum_{j=1}^n \sum_{j'=1}^n \frac{1}{4\pi\epsilon_0} \frac{e^2}{|r_j - r_{j'}|} \end{aligned} \quad (3.2)$$

Where  $T_N$  and  $T_e$  are kinetic energy operators of nucleus and electron, respectively.  $V_{NN}$ ,  $V_{Ne}$  and  $V_{ee}$  are potential operators of nucleus-nucleus interaction, nucleus-electron interaction, and electron-electron interaction, respectively. The kinetic operators can be explained as shown in equation (3.2), including  $\hbar = h/2\pi$ .  $M_i$  is the mass of nucleus and  $m_j$  is mass of an electron. The potential operators consist of  $Z_i$ ,  $R_i$ , and  $r_j$  which are atomic number of nuclei and position of nucleus and electrons, respectively. Solving the full Schrödinger equation with many particles is computationally challenging due to the complexity of the system. To simplify the

problem, the Born-Oppenheimer approximation (Born & Oppenheimer, 1927) is often applied. This approximation assumes that the motion of atomic nuclei and electrons occurs on vastly different time scales. Therefore, the motions of nuclei and electrons can be treated as decoupled, allowing the nuclei to be considered fixed while solving the electronic Schrödinger equation. Consequently, the Hamiltonian operator can be reduced as equation (3.3) based on the time-independent Schrödinger

$$\left( -\sum_{j=1}^n \frac{\hbar^2}{2m_j} \nabla_{r_j}^2 - \sum_{i=1}^N \sum_{j=1}^n \frac{1}{4\pi\epsilon_0} \frac{Z_i e^2}{|R_i - r_j|} + \frac{1}{2} \sum_{j=1}^n \sum_{j'=1}^n \frac{1}{4\pi\epsilon_0} \frac{e^2}{|r_j - r_{j'}|} \right) \Psi(\vec{r}_j) = E \Psi(\vec{r}_j) \quad (3.3)$$

The Born-Oppenheimer approximation can determine electronic energy level and wavefunctions, which form the basis of calculating a wide range of molecular properties. These include bond lengths, bond angles, vibrational frequencies, and other characteristics critical to understanding molecular systems.

### 3.2 Density functional theory

Density functional theory (DFT) is a quantum mechanical (QM) method widely used in chemistry and physics to calculate the electronic density of atoms, as shown in equation (3.4). This theory simplifies the approximation of Schrödinger equation instead of tracking individual particles within the system., offering a more computationally efficient alternative to the Hartree-Fock method. The electron density, expressed in terms of the wavefunction, represents a fundamental connection between the DFT method and the quantum mechanical description of electronic systems:

$$\rho(\vec{r}) = \sum_i \Psi_i^*(\vec{r}) \Psi_i(\vec{r}) = \sum_i |\Psi(\vec{r})|^2 \quad (3.4)$$

where  $\rho(\vec{r})$  represents the electron density at a given position  $\vec{r}$ , where interaction between electrons is not explicitly considered.

### 3.2.1 The Hohenberg-Kohn theorems

The Hohenberg-Kohn theorems (Hohenberg & Kohn, 1964a) developed by Pierre Hohenberg and Walter Kohn in 1964, are foundational principles in quantum mechanics and form the theoretical basis of DFT. The theorems consist of two key statements, often referred to as the first and second Hohenberg-Kohn theorems.

In case of first theorem, the external potential  $V(\mathbf{r})$  uniquely determines the ground-state electron density  $\rho(\mathbf{r})$ , and vice versa. In other words, knowing the external potential allows you to determine the electron density, and knowing the electron density allows you to reconstruct the external potential. This theorem forms the basis for expressing the total energy of a quantum system as a function of electron density,  $E[\rho]$ , and the external potential,  $V(\mathbf{r})$ . The main goal of DFT is to suggest the electron density which minimized the total energy. This energy is ground-state electron density and energy.  $\rho_0(\mathbf{r})$ ,

For the second theorem, it emphasizes the uniqueness of the ground-state electron density and the total energy of a quantum system. It describes a one-to-one correspondence between the ground-state electron density,  $\rho_0(\mathbf{r})$ , and the external potential,  $V_0(\mathbf{r})$ , which results in the same minimum value of the ground-state energy. In other words, a single ground-state electron density and its corresponding external potential uniquely minimize the total energy of the system. This relationship is mathematically represented as:

$$E[\rho_0(\mathbf{r})] = \frac{\partial E[\rho(\mathbf{r})]}{\partial \rho} \Big|_{\rho=\rho_0(\mathbf{r})} = \min_{\rho \rightarrow \rho_0} E[\rho(\mathbf{r})] \quad (3.5)$$

These theorems form the basis of DFT, which focuses on suggesting the electron density that minimizes the total energy functional of a quantum system. Although the Hohenberg-Kohn theorems do not provide a direct method for calculating the ground-state electron density, they offer a theoretical framework that ensures the accuracy and reliability of DFT in predicting the properties of many-electron systems.

### 3.2.2 The Kohn-Sham equation

The second Hohenberg-Kohn theorem provides the foundation for determining the ground-state energy of a quantum system by minimizing the total energy functional with respect to the electron density. In the framework of DFT, the total energy of a many-electron system is expressed as a functional of the electron density. This approach allows for the accurate prediction of ground-state properties without explicitly solving the many-body Schrödinger equation.

In the Kohn-Sham equation, a central component of DFT, the kinetic energy of electrons in a many-particle system is separated into two terms: (1) the kinetic energy of non-interacting electrons and (2) the contribution from electron-electron correlations, often referred to as the correlation effect on kinetic energy. This decomposition leads to the formulation of kinetic energy for electrons in a many-particle system as:

$$T[\rho(r)] = T_{non}[\rho(r)] + T_{cor}[\rho(r)] \quad (3.6)$$

For a system consisting of nuclei  $N$  and electrons  $N_e$ , the kinetic energy of non-interacting electrons can be represented as:

$$T_{non}[\rho(r)] = \sum_i^{N_e} \langle \psi_i(r) | \frac{-\nabla^2}{2} | \psi_i(r) \rangle \quad (3.7)$$

This term describes kinetic energy as if the electrons were moving independently, disregarding electron-electron interactions. However, in real systems, interactions between electrons significantly impact the total energy, necessitating the inclusion of potential energy terms. The potential energy contributions from electron-electron interactions and electron-nucleus interactions are given by:

$$V_{ee} = \langle \psi_e(r) | \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \frac{1}{|r_i - r_j|} | \psi_e(r) \rangle = \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' \quad (3.8)$$

$$V_{Ne} = \langle \psi_e(r) | \sum_i^N \sum_j^{N_e} \frac{-Z_i}{|R_i - r_j|} | \psi_e(r) \rangle = - \sum_{i=1}^N \int \frac{Z_i \rho(r)}{|R_i - r|} dr \quad (3.9)$$

These terms encapsulate the electrostatic forces within the system.  $V_{ee}$  accounts for the repulsive interactions between electrons, while  $V_{Ne}$  describes the attractive forces between electrons and nuclei. Together, these terms are crucial for determining the system's total energy.

In the Hartree-Fock approximation, the exchange energy naturally arises from the antisymmetric nature of electron wavefunctions, a consequence of the Pauli exclusion principle. However, this approximation neglects the correlation energy, which represents the additional energy associated with the dynamic interactions between electrons. To overcome this limitation, DFT combines both the exchange and correlation energy into a single term known as the exchange-correlation energy, denoted as:

$$E_{xc}[\rho(r)] = E_x[\rho(r)] + E_c[\rho(r)] \quad (3.10)$$

This unified term allows DFT to incorporate both effects seamlessly, improving accuracy over the Hartree-Fock method. The total energy of a many-particle system in DFT is expressed as:

$$E[\rho(r)] = T_{non}[\rho(r)] + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' - \sum_{i=1}^N \frac{Z_i \rho(r)}{|R_i - r|} dr + E_{xc}[\rho(r)] \quad (3.11)$$

According to the second Hohenberg-Kohn theorem, the ground-state energy of a quantum system corresponds to the minimum value of this energy functional. The condition for achieving this minimum is given by:

$$\left[ -\frac{\nabla_i^2}{2} + V_{eff}[\rho(r)] \right] \psi_i^{KS}(r) = E_i \psi_i^{KS}(r) \quad (3.12)$$

The effective potential in the Kohn-Sham equation, which governs the behavior of the electrons, can be written as:

$$\begin{aligned} V_{eff}[\rho(r)] &= V_H[\rho(r)] + V_{ext}[\rho(r)] + V_{xc}[\rho(r)] \\ &= \frac{1}{2} \int \frac{\rho(r')}{|r - r'|} dr' - \sum_{i=1}^N \frac{Z_i}{|R_i - r|} + V_{xc}[\rho(r)] \end{aligned} \quad (3.13)$$

This effective potential includes contributions from the external potential, the Hartree potential (arising from electron-electron interactions), and the exchange-correlation potential, which incorporates quantum mechanical corrections. By solving the Kohn-Sham equations iteratively, the ground-state electron density and corresponding energy of the system can be determined. This methodology makes DFT a powerful tool for studying the electronic structure of complex systems, bridging the gap between computational efficiency and physical accuracy.

### 3.2.3 Exchange-correlation functional

For DFT calculations, the exchange-correlation potential (XC) accounts for all quantum mechanical interactions and effects that are not included in other potentials in density functional theory (DFT). The XC operator is a critical yet challenging component of DFT because its exact form remains unknown. Although XC energy typically constitutes less than 10% of the total energy, it plays a vital role in determining the properties of materials in DFT calculations.

In the present day, various approximations of the XC functional have been proposed, including the local density approximation (LDA) and the generalized gradient approximation (GGA). The local XC energy per electron can be expressed as:

$$\varepsilon_{XC}[\rho(\vec{r})] = \frac{1}{2} \int \frac{\rho_{XC}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (3.14)$$

Then

$$E_{XC}[\rho(\vec{r})] = \int \rho(\vec{r}) \varepsilon_{XC}(\vec{r}, \rho) d\vec{r} \quad (3.15)$$

For the LDA, the XC functional is exactly for a homogeneous electron gas. The XC energy for the LDA can be written as:

$$E_{XC}^{LDA}[\rho(\vec{r})] = \int \rho(\vec{r}) \varepsilon_{XC}^{LDA}[\rho(\vec{r})] d\vec{r} \quad (3.16)$$

Nevertheless, the LDA has imitations in accurately describing systems with varying electron densities (inhomogeneous), making it less suitable for real systems with complex electronic structures. To overcome these limitations, GGA incorporates

the density gradient, allowing it to account for inhomogeneous behavior more effectively. The general formula for the XC energy in GGA is given by:

$$E_{XC}^{GGA}[\rho(\vec{r})] = \int \rho(\vec{r}) \varepsilon_{XC}^{GGA}[\rho(\vec{r}), \nabla\rho(\vec{r})] d\vec{r} \quad (3.17)$$

GGA functionals are widely used due to their accuracy for a range of properties, including ground-state energies, molecular geometries, and covalent bonding. They are also well-suited for weakly bonded systems (Santra et al., 2007). Currently, several forms of GGA functionals have been developed, including PW91 (Perdew & Wang, 1992), PBE (Perdew et al., 1996). In our work, the PBE functional is mainly used due to its balance of accuracy and computational efficiency. The PBE functional can be written as:

$$\varepsilon_{XC}^{PBE}[\rho(\vec{r}), \nabla\rho(\vec{r})] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} n^{\frac{1}{3}}(\vec{r}) F(x) \quad (3.18)$$

where

$$F(x) = 1 + a - \frac{a}{1+bx^2}, \quad x = \frac{|\nabla\rho(\vec{r})|}{n^{\frac{4}{3}}(\vec{r})} \quad (3.19)$$

Where  $a$  and  $b$  are constants. Substituting equation (3.19) into equation (3.20), the corresponding XC potential for PBE is:

$$V_{XC}^{PBE}[\rho(\vec{r})] = \frac{\delta E_{XC}^{PBE}[\rho(\vec{r})]}{\delta\rho(\vec{r})} \quad (3.20)$$

The PBE functional's ability to incorporate density gradients while maintaining computational simplicity makes it a popular choice for a wide range of applications in materials science and quantum chemistry.

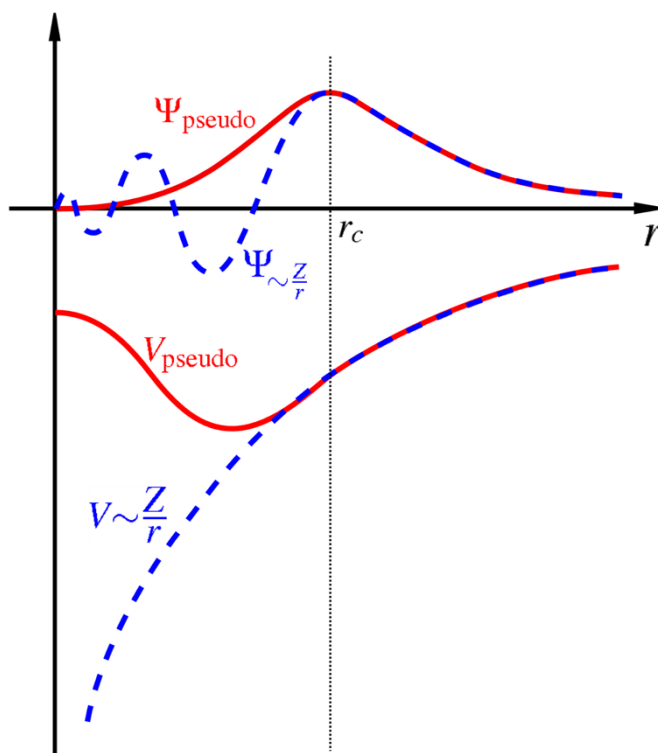
### 3.2.4 Pseudopotentials

Pseudopotentials are an essential tool for simplifying complex calculations in computational chemistry. They replace the true potential of atomic nuclei with an effective potential designed to replicate the behavior of valence (outermost) electrons, while either simplifying or neglecting the contributions of tightly bound inner-core electrons. In most cases, bond formation and electronic properties are determined by valence electrons, while core electrons are treated as part of the nuclei under the frozen-core approximation. This method simplifies the description of pseudo-

wavefunctions and facilitates the practical use of plane-wave basis sets. Additionally, this simplification significantly reduces the computational cost of electronic structure calculations while maintaining accuracy for many properties of interest.

As shown in Figure 3.1, the pseudo and exact potential align when the interparticle distance exceeds the specified cutoff radius ( $r_c$ ). Similarly, the pseudo ( $\psi_{pseudo}$ ) and exact ( $\psi_{exact}$ ) wavefunctions also converge beyond this radius. Within the region below  $r_c$ , however, the exact wavefunction exhibits pronounced oscillations. These oscillations make solving the Schrödinger equation challenging, as achieving a smooth and numerically stable wavefunction in this region requires significant computational effort, as shown by the red solid line in the figure.

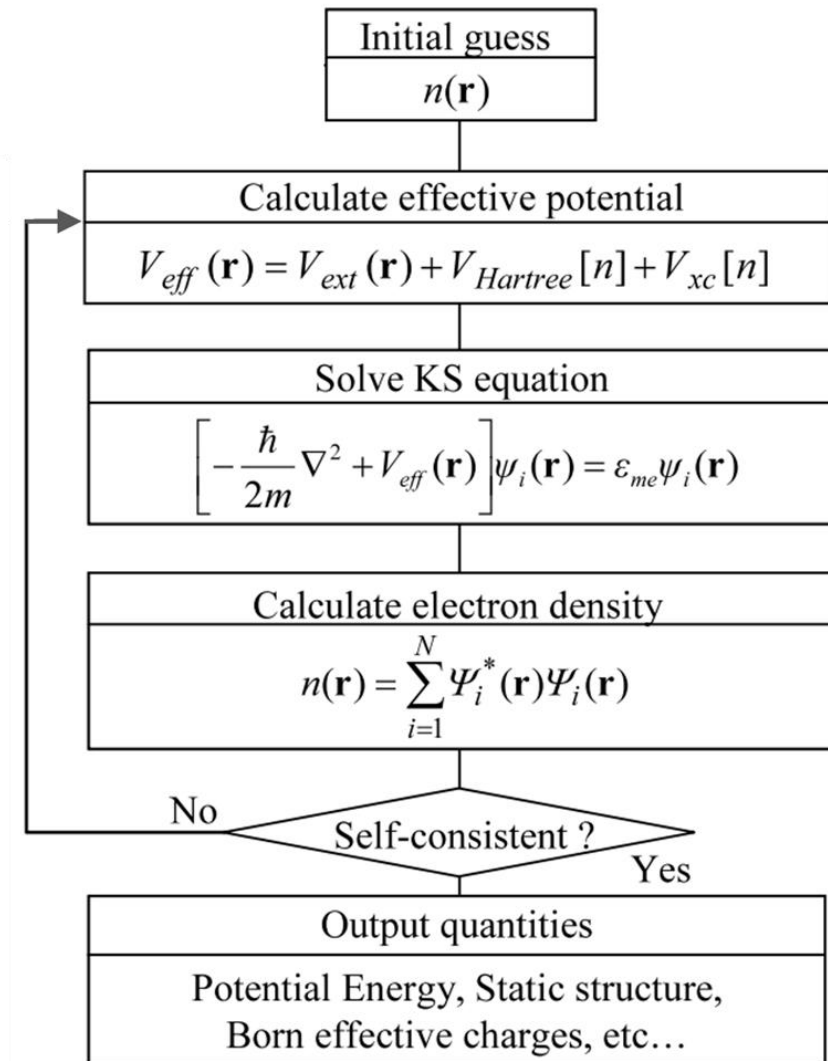
To overcome this issue, a smoother pseudo-wavefunction is employed, which significantly reduces computational cost while maintaining accuracy. For the pseudo wavefunction and potential to be effective, they must satisfy the following criteria: (1) Consistency: The pseudo wavefunction and potential should match the exact counterparts beyond the cutoff radius. (2) Smoothness: Within the  $r_c$  region, the pseudo wavefunction should minimize oscillations to simplify numerical calculations. (3) Transferability: The pseudopotential should accurately describe the behavior of valence electrons across various chemical environments. These requirements ensure that pseudopotentials serve as an efficient and accurate approach to simplifying electronic structure calculations (Kresse & Joubert, 1999).



**Figure 3.1** Comparison of wavefunctions in a nuclear Coulomb potential (blue) and a pseudopotential (red) (Grajcarova, 2013).

### 3.2.5 Self-consistent field approach

In practical DFT calculations, the ground-state energy of a many-body system is determined using a self-consistent field (SCF) method. This approach focuses on finding the lowest-energy configuration of atoms by solving the Kohn-Sham equation. Figure 3.2 presents the flowchart of this process, ensuring that the electron density and effective potential reach a stable and consistent solution.



**Figure 3.2** Flowchart showing the process of solving the Kohn-Sham equation (Nakamachi et al., 2013).

The SCF calculation follows a systematic process to determine the ground-state energy in density functional theory (DFT) calculations. The steps involved are as follows:

1. Initial electron density guess: make an initial assumption for the electron density
2. Effective potential calculation: compute the effective potential using the initial electron density
3. Solving the Kohn-Sham equation: Solve the Kohn-Sham equation to suggest the eigenvalues (total energy) and eigenvectors (wavefunctions)

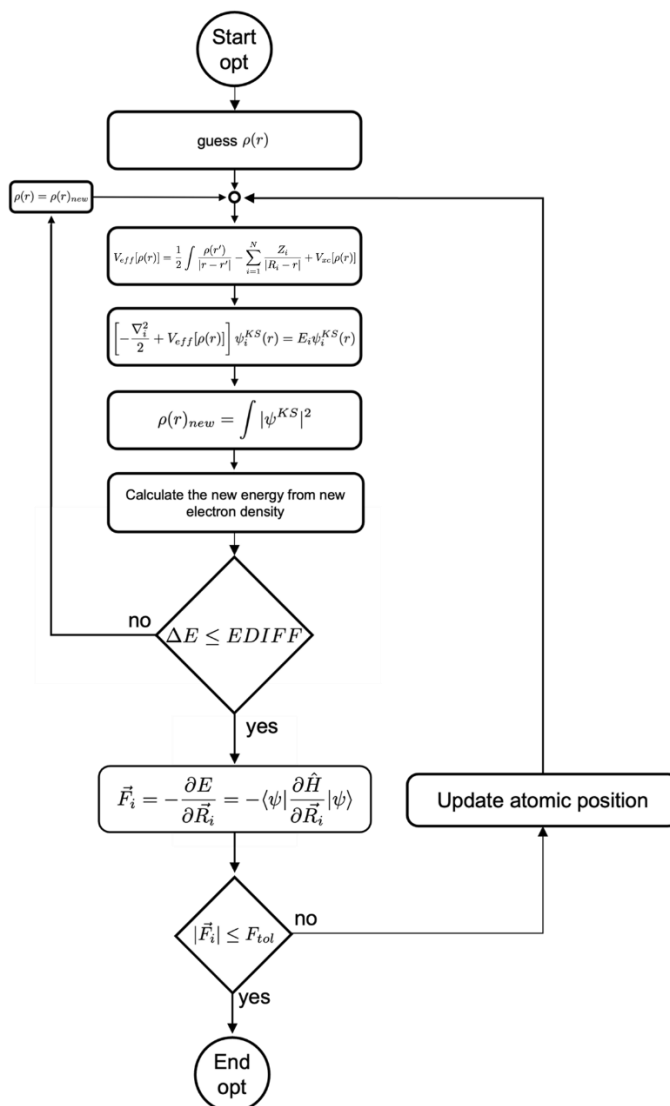
4. New electron density calculation: Generate a new electron density based on the calculated eigenvectors (wavefunctions).
5. New energy calculation: Calculate the total electronic energy using the updated electron density in the Kohn-Sham equation
6. Energy convergence check: if the difference between the new and previous electronic energy is smaller than the predefined convergence criterion, the calculation terminates, and the resulting values are accepted. However, If the difference exceeds, update the electron density with the new values and repeat the process from step 2. This process is repeated until the calculated energy and electron density reach convergence, ensuring a consistent solution for the electron density and effective potential. In this thesis, the convergence criterion is set to  $10^{-6}$  eV.

### 3.3 Geometry optimization

Geometry optimization is a critical step in DFT calculations, particularly for studying molecules and materials. The goal is to find the most energetically favorable arrangement of atoms by minimizing the system's total energy while adjusting atomic positions and, if applicable, unit cell dimensions. An overview of the geometry optimization process is provided below (see Figure 3.3). First step, it is initial geometry which starts with the initial atomic coordinate of the system. Next, the DFT calculation determines the system's total energy using the self-consistent field (SCF) method and further calculates the atomic forces using the Hellmann-Feynman theorem. In case of convergence check after calculations, If the calculated atomic forces are below the predefined tolerance limit, the optimization is complete, and the resulting geometry is accepted. However, If the atomic forces exceed the tolerance limit, the atomic positions are adjusted based on the calculated forces and gradients. The optimization process then returns to step 2, iterating until convergence is achieved. Optimization algorithms, such as the conjugate gradient method, are typically used to guide the adjustments (Dai et al., 2017).

Geometry optimization is a foundational process in DFT that allows for accurate predictions of molecular and material properties. This method offers critical insights

into the behavior, stability, and structural characteristics of chemical systems by calculating the optimal atomic positions and total energy.



**Figure 3.3** Schematic representation of the optimization process in DFT calculations.

### 3.4 vdW correction

One of the well-known limitations of DFT is its inability to accurately capture van der Waals (vdW) interactions. These interactions are weak, long-range forces between molecules or atoms that result from temporary fluctuations in electron density. Standard DFT functionals, including LDA and GGA, are designed to capture local exchange-correlation effects but frequently underestimate vdW interactions.

To overcome this limitation, various correction methods have been developed to incorporate vdW interactions into DFT calculations. One widely used approach is the DFT-D3 method developed by Grimme (Grimme et al., 2010). DFT-D3 is an empirical correction method, to account for long-range van der Waals (vdW) interactions. Standard DFT functionals often fail to capture these non-covalent forces, which are critical for describing many systems (e.g., molecular crystals, protein folding, adsorption). As defined in the paper, the total energy is the sum of the standard DFT energy and the dispersion correction:

$$E_{\text{DFT-D3}} = E_{\text{KS-DFT}} + E_{\text{disp}} \quad (3.21)$$

The dispersion term,  $E_{\text{disp}}$ , consists of a two-body term ( $E_2$ ) and an optional three-body term ( $E_3$ , which is often omitted). The primary  $E_2$  term, which truncates the full series at  $n = 8$ , is:

$$E_{\text{disp}} \approx E^{(2)} = - \sum_{i=1}^{N_{\text{at}}} \sum_{j=i+1}^{N_{\text{at}}} \sum_{\mathbf{L}} \left( s_6 f_{d,6}(r_{ij,\mathbf{L}}) \frac{C_{6ij}}{r_{ij,\mathbf{L}}^6} + s_8 f_{d,8}(r_{ij,\mathbf{L}}) \frac{C_{8ij}}{r_{ij,\mathbf{L}}^8} \right) \quad (3.22)$$

Where:

- $\sum_{i=1}^{N_{\text{at}}} \sum_{j=i+1}^{N_{\text{at}}} \dots$  This is a sum over all unique atom pairs in the system, which contains  $N_{\text{at}}$  atoms. (This notation, summing  $j$  from  $i + 1$ , is a computationally efficient way to sum each pair only once).
- $\sum_{\mathbf{L}}$  This is the summation over lattice vectors,  $\mathbf{L}$ . This component is only used for periodic systems (like crystals or surfaces). It ensures that atom  $i$  interacts not only with atom  $j$  in the primary unit cell but also with all of its periodic images in adjacent cells. For an isolated molecule, this summation is absent.
- $s_6$  and  $s_8$  (Global Scaling Factors) These are the key empirical parameters of the D3 method. Each density functional (like PBE, B3LYP, etc.) has its own pair of  $s_6$  and  $s_8$  values, which are determined by fitting to a benchmark set of high-accuracy reference energies. These parameters "tune" the correction to seamlessly merge

with the short-range correlation already provided by the specific DFT functional. As the paper states,  $s_8$  is often the main adjustable parameter.

- $C_{6ij}$  and  $C_{8ij}$  (Dispersion Coefficients) These are the  $n=6$  (dipole-dipole) and  $n=8$  (dipole-quadrupole) dispersion coefficients for the atom pair  $(i, j)$ . A key innovation of D3 is that these coefficients are not static. They are calculated "on the fly" based on the coordination number (CN) of each atom in its specific molecular environment. This makes D3 far more accurate than previous methods, as the coefficients adapt to the atom's local chemistry.
- $r_{ij,L}$  (Interatomic Distance) This is the distance between atom  $i$  and atom  $j$  (or its periodic image,  $L$ ).
- $f_{d,n}(r_{ij,L})$  (The Damping Function) This function is critical for preventing "double counting" and unphysical behavior. It smoothly turns off the dispersion correction ( $f \rightarrow 0$ ) at short interatomic distances, where atoms are covalently bonded. It ramps up to ( $f \rightarrow 1$ ) at larger distances, turning the correction "on" only where it's needed (i.e., in the non-covalent, long-range region).

### 3.5 Climbing image-nudged elastic band method

The climbing image-nudged elastic band (CI-NEB) (Henkelman et al., 2000) is an advanced computational technique widely used in DFT calculations to suggest transition states and map reaction pathways with precision. By enhancing the traditional Nudged Elastic Band (NEB) method, CI-NBE introduces a "climbing" image that converges toward the transition state, allowing for precise determination of the highest energy points along a reaction coordinate. Next, paraphrase will summarize knowledge of these methods.

In the case of NEB, it can calculate the reaction pathway by constructing a series of intermediate configurations (called images) that connect the initial and final states. Each image is characterized by specific atomic coordinates, forming an elastic band represented as  $[R_0, R_1, R_2, \dots, R_N]$ , where  $R_0$  and  $R_N$  remain fixed as the initial and final state. The force acting on each image ( $F_i$ ) is a combination of spring force and true force. Spring force is used to ensure images remain evenly spaced along the reaction

path. True force is used to account for the system's potential energy, acting perpendicular to the reaction path. The total force for an image  $i$  is expressed as:

$$\vec{F}_i^{NEB} = \vec{F}_i^{s||} - \nabla E(\vec{R}_i)^\perp \quad (3.23)$$

The true force is given by:

$$\nabla E(\vec{R}_i)^\perp = \nabla E(\vec{R}_i) - \nabla E(\vec{R}_i) \cdot \hat{\tau}_i \quad (3.24)$$

Where  $\nabla E$  is the gradient of energy with respect to atomic coordinates, and  $\hat{\tau}_i$  is the normalized local tangent at image  $i$ . Spring force is defined as:

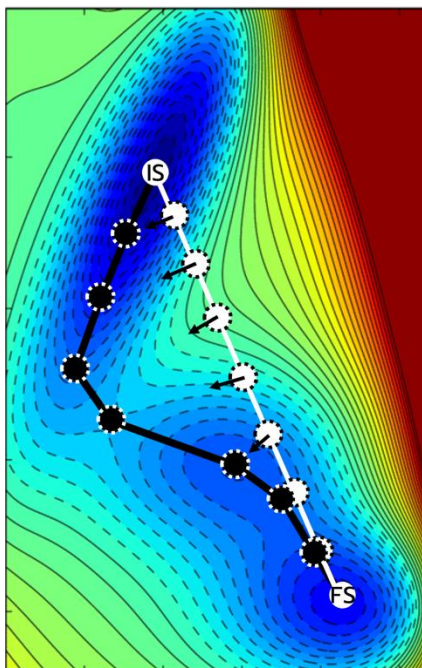
$$\vec{F}_i^{s||} = k(|\vec{R}_{i+1} - \vec{R}_i| - |\vec{R}_i - \vec{R}_{i-1}|)\hat{\tau}_i \quad (3.25)$$

Where  $k$  is spring constant. Optimization algorithms move the images according to NEB force until the forces converge below a set threshold. In our study, we set the convergence criterion for NEB calculations which is 0.05 eV/Å

The CI-NBE method improves upon NEB by refining the transition state suggestion. After several iterations with the standard NEB, the image with the highest energy ( $i_{max}$ ) is identified. This image is then allowed to "climb" toward the saddle point by modifying its force calculation:

$$\vec{F}_{i_{max}} = -\nabla E(\vec{R}_{i_{max}}) + 2\nabla E(\vec{R}_{i_{max}}) \cdot \hat{\tau}_{i_{max}} \quad (3.26)$$

This modification ensures that the climbing image is unaffected by spring forces and moves directly to the saddle point, representing the transition state. Consequently, the CI-NEB method is widely used in computational chemistry to study reaction mechanisms and calculate energy barriers for chemical reactions. It delivers three key benefits by determining the transition state with accuracy, mapping minimum energy pathways precisely, and providing insights into the reaction dynamics of complex systems.



**Figure 3.4** Schematic of the potential energy surface (PES) and NEB calculation, showing the initial reaction pathway (white line) and the optimized reaction pathway (black line).

Overall, the CI-NEB method combines the principles of the NEB method with the climbing image adjustment, providing an efficient and reliable approach for identifying transition states and understanding reaction mechanisms. By ensuring accurate placement of the transition state along the reaction coordinate, CI-NEB is a critical tool for investigating complex chemical reactions and energy landscapes.

### 3.6 Gibbs free energy ( $G$ ) calculation

The Gibbs free energy ( $G$ ) can be expressed as the sum of the system's enthalpy ( $H$ ) and entropy ( $S$ ), as shown below:

$$G = E_{elec} + E_{ZPE} - TS \quad (3.27)$$

Here,  $E_{elec}$  represents electronic energy, and  $E_{ZPE}$  is the zero-point energy correction applied to the electronic energy to account for quantum mechanical effects at absolute zero. The zero-point energy is calculated as:

$$ZPE = \sum_i \frac{h\nu_i}{2} \quad (3.28)$$

where,  $h$  is the Planck's constant and  $\nu_i$  are the computed vibrational frequencies of the system. This correction is essential in ensuring accurate thermodynamic predictions, especially for molecular systems at low temperatures. For entropy ( $S$ ), it is given by the equation:

$$S = k_B \ln Q \quad (3.29)$$

The partition function ( $Q$ ) can be expressed as the product of translational, rotational, and vibrational components:

$$Q = f_{trans} f_{vib} f_{rot} \quad (3.30)$$

In equation (3.30), The calculation of entropy relies on the partition function, which for ideal gas molecule can be divided into translational, rotational, and vibrational contributions. Each component corresponds to a specific type of motion or degree of freedom within the system. For a free-gas molecule, the translational partition function in three dimensions is given by:

$$f_{trans} = V \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} \quad (3.31)$$

where  $V$  is the volume of the gas,  $M$  is the molecular mass,  $k_B$  is the Boltzmann constant. Often,  $V$  can be substituted using the ideal gas equation of state  $PV = k_B T$ . For a single dimension, the translational partition function simplifies to:

$$f_{trans} = \frac{L \sqrt{2\pi m k_B T}}{h} \quad (3.32)$$

Where  $L$  is the characteristic length along one dimension. In case of the rotational partition function for a diatomic molecule can be expressed as:

$$f_{rot} = \frac{8\pi^2 I k_B T}{h^2} \quad (3.33)$$

Where  $I$  is the moment of inertia about an axis perpendicular to the molecular axis and passing through the center of mass.

In the harmonic approximation, the vibrational partition function is given as:

$$f_{vib} = \frac{1}{1 - e^{-\hbar\omega/k_b T}} \quad (3.34)$$

Each vibrational mode contributes independently to the partition function, and the harmonic approximation assumes that the vibrations are small perturbations around equilibrium.

### 3.7 Smooth Overlap of Atomic Positions (SOAP)

The Smooth Overlap of Atomic Positions (SOAP) descriptor has been extensively studied and applied in computational materials science and chemistry (Bartók et al., 2013). It was introduced as a method to represent atomic neighborhood environments, ensuring differentiability and invariance to fundamental symmetries, making it particularly suitable for analyzing structural similarities in materials. SOAP has been widely used for fitting potential energy surfaces, optimizing machine learning interatomic potentials, and improving predictive modeling in various applications, including drug design and materials characterization. Additionally, SOAP descriptors have been employed for mapping atomic coordinates to electron densities, demonstrating their effectiveness in predicting charge distributions in different systems. These studies underscore the versatility and efficacy of SOAP in characterizing atomic environments and predicting material properties.

SOAP achieves its structural representation by constructing a continuous atomic density function, where atomic positions are expressed as Gaussian functions centered at each atom. Mathematically, this is given by:

$$\rho_i(\mathbf{r}) = \sum_j \exp\left(-\frac{|\mathbf{r} - \mathbf{r}_j|^2}{2\sigma^2}\right) f_{cut}(|\mathbf{r} - \mathbf{r}_j|) \quad (3.35)$$

where  $\rho_i(\mathbf{r})$  represents the atomic density around atom  $i$ ,  $\sigma$  is the Gaussian broadening parameter, and  $f_{cut}(\mathbf{r})$  is a cutoff function ensuring that only atoms within a distance  $r_{cut}$  contribute to the density. The cutoff function smoothly decays atomic contributions at large distances:

$$f_{cut}(r) = \left(1 - \frac{r}{r_{cut}}\right)^n \quad (3.36)$$

where  $r_{cut}$  is the cutoff radius, defining the spatial range of atomic interactions.

To make the density function computationally manageable, it is expanded using radial basis functions  $g_n(r)$  and spherical harmonics  $Y_{lm}(\theta, \phi)$ , resulting in:

$$\rho_i(r) = \sum_{nlm} c_{nlm} g_n(r) Y_{lm}(\theta, \phi) \quad (3.37)$$

where  $g_n(r)$  captures radial features, controlled by the maximum number of radial basis functions ( $n_{max}$ ), and  $(Y_{lm}(\theta, \phi))$  describes angular features, determined by the maximum angular momentum ( $l_{max}$ ). The expansion coefficients, computed as:

$$c_{nlm} = \int \rho_i(r) g_n(r) Y_{lm}(\theta, \phi) dr \quad (3.38)$$

numerically encode the atomic environment into a descriptor vector.

To ensure rotational invariance, SOAP descriptors are constructed using the power spectrum:

$$p_{nn'l} = \sum_m c_{nlm} c_{n'l m}^* \quad (3.39)$$

This power spectrum forms a unique fingerprint of the atomic neighborhood, allowing for robust structural comparisons independent of orientation.

To gain deeper insight into the correlation between structural changes, adsorption behavior, and deformation energy, SOAP analysis was employed to quantify structural similarity before and after adsorption. The SOAP similarity score (Similarity) is calculated using the following equation

$$\text{Similarity} = \left( \frac{X_{\text{initial}} \cdot X_{\text{final}}}{\|X_{\text{initial}}\| \cdot \|X_{\text{final}}\|} \right)^\zeta \times 10 \quad (3.40)$$

Where,  $X_{\text{initial}}$  represents the SOAP descriptor vector for the initial (reference) structure, and  $X_{\text{final}}$  is the SOAP descriptor vector for the final (adsorbed) structure. The terms  $\|X_{\text{initial}}\|$  and  $\|X_{\text{final}}\|$  denote the magnitudes of these vectors, ensuring the similarity

is normalized. (set to 4 in this study) amplifies the similarity value. This equation computes the cosine similarity between the SOAP vectors and scales the result from 0 to 10, with a score close to 10 indicating minimal structural change and high stability.

The SOAP descriptor provides an effective and numerically stable means of quantifying local atomic environments, making it a widely used tool in computational materials science. By incorporating SOAP into adsorption studies, it becomes possible to systematically compare structural distortions and gain insight into the stability and interaction strength of adsorbed species.

### 3.8 Crystal orbital Hamilton population (COHP)

The crystal orbital hamilton population (COHP) is a theoretical method used in computational chemistry and materials science to suggest chemical bonding in periodic systems (Steinberg & Dronskowski, 2018). It is particularly effective in quantifying the bonding, nonbonding, and antibonding interactions between atomic orbitals in solids. The fundamental concept of COHP focused on partitioning the electronic structure of a system into contributions from specific atomic pairs or orbitals. It combines concepts from quantum mechanics and electronic structure theory, particularly the Hamiltonian formalism, to analyze the interaction between two atomic orbitals.

COHP is often evaluated relative to the Fermi level, which suggests the energy up to which the electronic states are occupied. The bonding interactions below the Fermi level are most significant in determining the stability of the system.

It can be calculated based on electronic Hamiltonian ( $\hat{H}$ ) describes the total energy of the quantum system, including kinetic and potential energies. In COHP, it is used to evaluate the interaction between two atomic orbitals:

$$H_{ij} = \int \psi_i^*(\mathbf{r}) \hat{H} \psi_j(\mathbf{r}) d^3r \quad (3.41)$$

The term of Hamilton population quantifies the contribution of each orbital pair to the total electronic energy:

$$HP_{ij}(E) = -H_{ij}(E) \cdot n_{ij}(E) \quad (3.42)$$

After that, COHP is derived by integrating over all energy states:

$$-COHP(E) = - \sum_{i,j} H_{ij}(E) \cdot n_{ij}(E) \quad (3.43)$$

The negative value of COHP represents bonding contributions, whereas positive values show antibonding contributions. To obtain a single scalar value representing the total bonding interaction between two atoms, COHP can be integrated over all relevant energy levels:

$$ICOHP = \int_{E_{\min}}^{E_F} -COHP(E) dE \quad (3.44)$$

ICOHP value can suggest the bonding strength. Negative ICOHP suggests strong bonding interactions, while positive value suggest dominant antibonding interactions. Although COHP and ICOHP can explain the strength bond of pair atoms, it still has limitations which we should be concerned about. First, it is basis set dependence. Results can vary with the choice of basis sets, requiring careful validation. Computational cost increases with system size, especially for large supercells or complex systems. Lately, the choice of integration limits in ICOHP calculations can influence the results, particularly in systems with partially filled bands.

### 3.9 Summary of computational details

In this thesis, all calculations were employed using spin-polarized Density Functional Theory (DFT) (Hohenberg & Kohn, 1964b) as implemented in the Vienna Ab-initio Simulation Package (VASP 6.3) (Kresse & Furthmüller, 1996b, 1996a). The frozen-core projector-augmented wave (PAW) method was used to describe the electron-ion interactions (Blöchl, 1994). For the  $V_2CO_2$  structure, valence electrons included V 3d4s, C 2s2p, and O 2s2p treated within a plane-wave basis. For  $S_8$  and  $Al_2S_n$  species, Al 3s3p and S 3s3p valence electrons were considered. Screening of single-atom (SA) transition metals included 3d-transition metals, considering their 3d4s valence electrons, respectively. The exchange-correlation interactions were approximated using the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional (Kresse & Joubert, 1999; Perdew et al., 1996). Weak van der Waals

interactions between the adsorbates ( $S_8$  and  $Al_2S_3$ ) and the decorated 3d-TMs on  $V_2CO_2$  were included using the DFT-D3 (Grimme et al., 2010, 2011). Structural optimizations were carried out with a kinetic energy cutoff of 500 eV. Monkhorst-Pack k-point sampling was employed (Monkhorst & Pack, 1976), using a  $3 \times 3 \times 1$  grid for structural optimization and a  $5 \times 5 \times 1$  grid for electronic density of states (DOS) calculations. Optimization was considered complete when the energy difference between iterations reached  $10^{-6}$  eV and residual forces were below 0.02 eV/Å. Charge distribution analysis was conducted using the Bader charge decomposition scheme. The energy barriers and reaction pathways for the decomposition of  $Al_2S_3$  was calculated using the Climbing Image Nudged Elastic Band (CI-NEB) method (Henkelman et al., 2000)

### 3.10 References

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