First-principles calculations, also known as ab initio calculations, are indispensable tools in understanding the properties and behavior of materials at the atomic and molecular level. These calculations involve the computation of various energies to gain insights into material stability and formation. Three critical energies frequently calculated are formation energy, cohesive energy, and binding energy. In this blog post, we will explore the definitions of these energies and examine their calculations, providing a clear understanding along with practical examples.

Formation Energy

Formation energy represents the change in energy that occurs when a material is formed from its constituent elements in their reference states. It quantifies the stability and likelihood of formation for a given compound. The formation energy of a material can be computed by taking the difference between the total energy of the compound and the sum of the energies of its constituent elements in their respective reference states.

Example: Let's consider the formation energy of alumina (Al_2O_3). To calculate this, we compare the total energy of Al_2O_3 with the sum of the energies of fcc aluminum and O_2 gas in their reference states. The formation energy (FE) can be determined as follows:

$FE(Al_2O_3)$ = Total energy of Al_2O_3 – (Total energy of fcc Al + Total energy of O_2 gas)

Cohesive Energy

Cohesive energy measures the amount of energy required to break a material into isolated atoms or ions. It reflects the strength of the interactions holding the material together. Cohesive energy is also referred to as atomization energy. Calculating cohesive energy involves determining the total energy of the material and comparing it with the sum of the energies of its constituent isolated atoms or ions.

Example: Let's consider the cohesive energy of a simple crystal, such as ZnS (zinc blende phase). In this case, we calculate the total energy of the zinc-sulfide crystal and the total energies of isolated zinc and sulfur atoms. The cohesive energy (CE) is determined as follows:

CE = Total energy of ZnS crystal – (Total energy of isolated Zn atom + Total energy of isolated S atom)

The above formula assumes a primitive unit cell is used for ZnS crystal, which contains a single Zn and a single S atom. If one uses a conventional unit cell with 4 Zn and 4 S atoms, then the formula would be

CE = Total energy of ZnS crystal – (4 × Total energy of isolated Zn atom + 4 × Total energy of isolated S atom)

Binding Energy

Binding energy refers to the amount of energy required to separate the constituent parts of a system, which can have different meanings depending on the context. When discussing molecules, binding energy often refers to atomization energy—the energy needed to dissociate a molecule into its constituent atoms. Binding energy quantifies the strength of the bonds within a molecule.

Example: Consider a water molecule (H_2O). The binding energy of H_2O can be calculated by subtracting the total energy of the isolated hydrogen atoms and oxygen atom from the total energy of the H_2O molecule.

Binding Energy(H_2O) = Total energy of H_2O – (Total energy of isolated H atom) × 2 – Total energy of isolated O atom

References

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