ab initio Computational Materials Science

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Abstract

The aim of quantum chemistry is the solution of Schrödinger´s Equation, $\hat{H}\,\Psi = E\,\Psi$, "from first principles" (*ab initio*), that is, without empirical adjustments.
The wave function $\Psi = \Psi(R_i, r_i, t)$ describes the entire atomic-like system and essentially all properties can be derived from Ψ, such as chemical constitution, configuration and bonding, structures, energies, forces etc.
Quantum-chemical calculations based on Density-Functional Theory (DFT) give access to the total energy of a system at constant volume, $E(V) \approx U(V)$. The enthalpy can be derived by calculating the total energy of the system at different volumes:

$$H(p) = E(V) + pV = E - \frac{\partial E}{\partial V}V \,.$$

The Gibbs free energy $G(p,T)$, which includes finite temperatures, can be obtained by including the influence of the lattice vibration, the so-called *phonons*,

$$G(p,T) = E(V) + F_{ph}(T,V) + pV \,,$$

where F_{ph} is the so-called Phonon Free Energy. What we would like to know are the phonon frequencies $\omega(\vec{k},\nu)$. They can be obtained from the forces acting on the atoms in the system when the atoms are slightly dislocated from their equilibrium positions. Other properties, such as heat capacity $C(T)$ and entropy $S(T)$, can also be calculated from the phonon frequencies.