

Types of Calculation

Stationary Point

In this type of calculation we give the software the geometry and calculate energy and other properties of interest. For example, a series of stationary point calculations could be used to assess the relative stabilities of a series of structures.

Available in:

- Molecular electronic structure – Gaussian, MOLPRO
- Periodic electronic structure – CRYTAL, CASTEP, CPMD, VASP
- Semi-empirical – Gaussian
- Molecular mechanics – Amber, DL_POLY

Geometry Optimization

A starting structure is provided and from this minimum energy structure is generated (the optimized geometry). This is done by calculating the forces between the atoms in the structure and adjusting the positions so as to minimize the forces and thus the potential energy of the system.

Instead of optimizing to a minimum energy structure you can also chose to optimize to a transition state or higher order saddle point on the potential energy surface. Careful use of geometry optimizations would allow you to characterise the potential energy surface for any system.

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- Periodic electronic structure - CRYSTAL
- Semi-empirical - Gaussian
- Molecular mechanics – Amber

Molecular Dynamics

A trajectory is followed through time from the starting structure. For molecular mechanics methods this is done by solving Newton's equations of motion for the system in question. For electronic structure methods we can follow a classical trajectory (where we solve Newton's equations for the motion of the nuclei but use the QM forces) or a quantum trajectory (using *path integral* methods).

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Vibrational Frequencies

The normal vibrational modes associated with a particular geometry can be generated by constructing the matrix of the second derivative of the energy (the *Hessian*) and diagonalizing it. The eigenvalues give the vibrational frequencies and the associated eigenvectors the atomic displacements associated with that mode.

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