UNIKASSEL VERSITÄT | BAUINGENIEUR UND UMWELT INGENIEURWESEN

From Electrons to Materials Properties

Density Functional Theory for Engineers and Materials Scientists

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Chapter VII

Car-Parrinello Molecular Dynamics and Metadynamics

Car-Parrinello MD

Like in classical MD, we take a Lagrangian and solve the Lagrangian equations of motion. Here, or Lagrangian has the form

(1) $$L = \frac{1}{2}\left(\sum_{A}^{N} M_A \dot{\boldsymbol{R}}_A^2 + \sum_{j}^{n} |\langle j|\nabla|j\rangle|^2\right) - E[\rho]$$

Note that the orthonormality constraint for orbitals is in action!

Now we just solve the resulting equations of motion

(2) $$M_A \ddot{\boldsymbol{R}}_A = -\nabla_A E[\rho]$$

(3) $$\dot{\boldsymbol{p}}_j = -\frac{\delta E[\rho]}{\delta \psi_j^*} + \sum_k \Lambda_{jk}\psi_k$$

What problems arise from this? How do we solve them?

- Run with small time steps
- Define a fictitious electron mass → slow down the electrons to stay in ground state
- Extrapolate the density development (within certain constraints)
- Re-run SCF every X steps

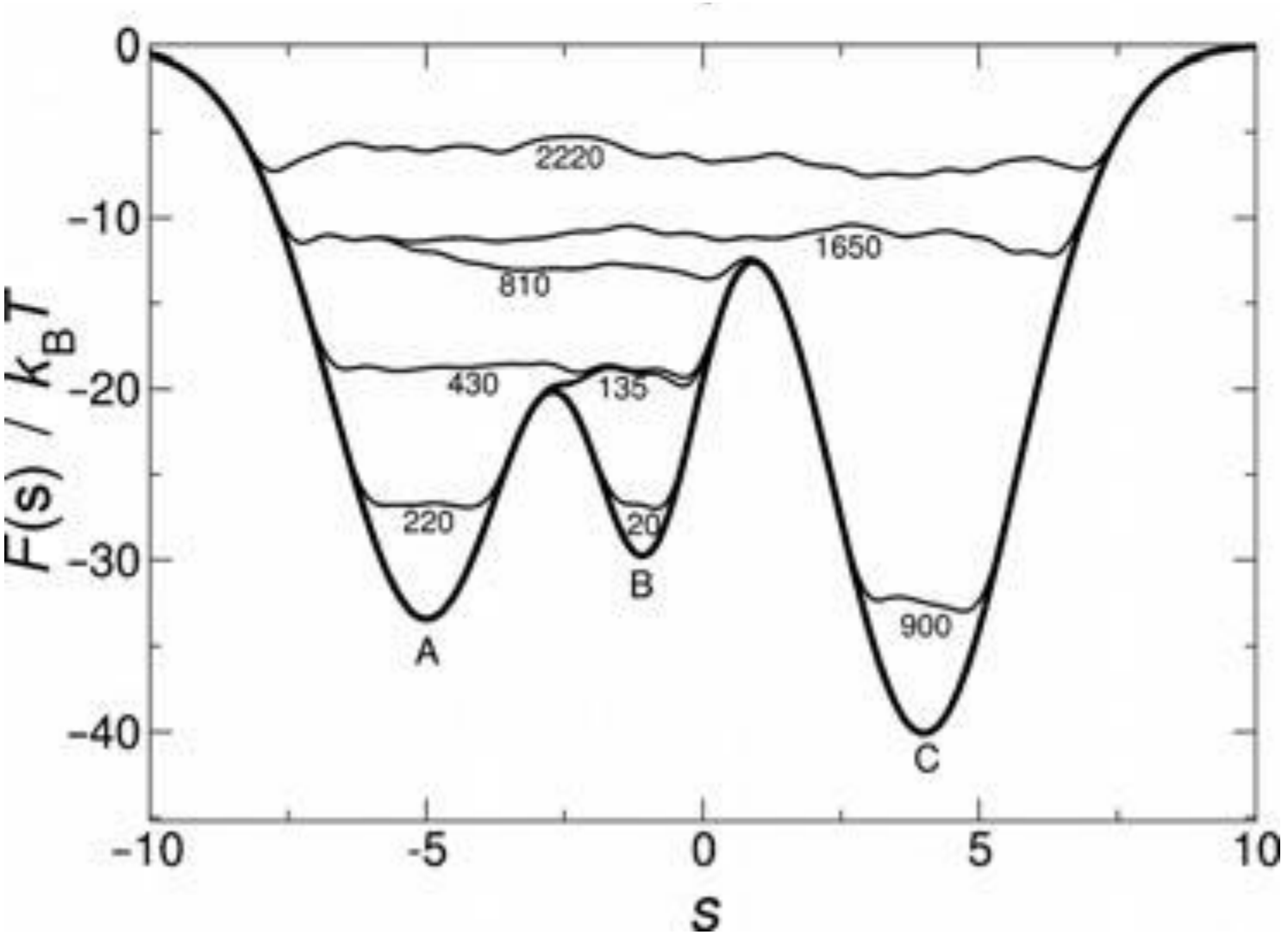
Metadynamics

Find rare events by biasing the PES.

First, we need to define a proper subset of variables, called collective variables, say $\{s_i\}$. Then, we can add a time-dependent bias potential of the form

$$V(\boldsymbol{s}, t) = \sum_{\tau<t} W(\tau) \exp\left(- \sum_i \frac{(s_i(t) - s_i(\tau))^2}{2\sigma_i^2} \right) \tag{4}$$

What happens if $t \to \infty$?


0
-10
-20
-30
-40
F(s) / k_B T
2220
1650
810
430
135
220
20
A
B
C
900
-10
-5
0
5
10
s

If $t \to \infty$ we obtain

(4) $$V(\boldsymbol{s}, t \to \infty) = -F + C$$

However, when truncating time we may be in trouble: