Constrained-DFT for diabatic PES mapping

The case of an H atom scattering from a Ge(111) surface

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1. Aim

During molecules-surface scattering, energy can be dissipated through the formation of electron-hole pairs. A curious case is the measured energy dissipation of H atoms scattering from a Ge(111) surface.
In this context, constrained DFT (cDFT) offers the possibility to calculate diabatic potential energy surfaces (PESs) in which the H atom has a fixed charge.

2. Constrained DFT

ABINIT allows to perform cDFT calculations using an algorithm where the constrained is introduced through Lagrangian multipliers. [1]

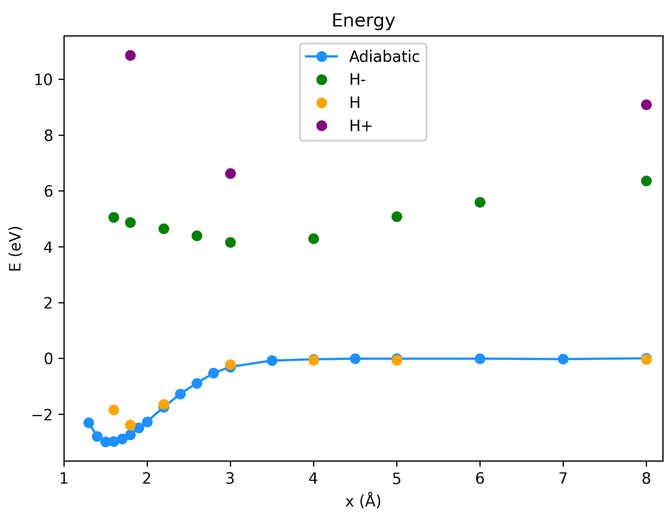
$$E_+^V[u,\Lambda] = E^V[u] + \Lambda(\rho_A^V[u] - N_A)$$

$$N_A \equiv \int w_A(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

A fragment A (represented as a sphere in the code) is considered, with an imposed charge N_A. w_A is a weight function, it's equal 1 inside the fragment and smoothly vanishes outside.

[1] X. Gonze *et al.* J. Chem. Theory Comput. **2022** 18 (10), 6099-6110

3. Diabatic PESs



By combining cDFT with charge analysis (paragraph 4), diabatic PESs associated with H in neutral (orange), anionic (green) and cationic (purple) states are obtained.
These values are displayed together with the adiabatic PES (blue), obtained without imposing any charge constraints.

Notes: PESs analysis was performed on a model system, a Ge(111) (2x2) surface cell, which is smaller that the well known Ge(111)c(2x8) reconstructed cell. Although these results can not be directly used to model the dynamics, they provide a qualitative understanding of the scattering event.

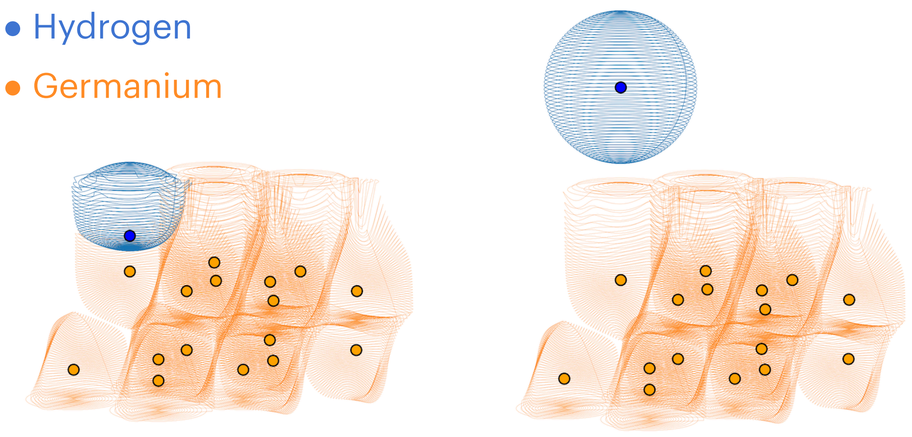
4. Quantum theory of atoms in molecules

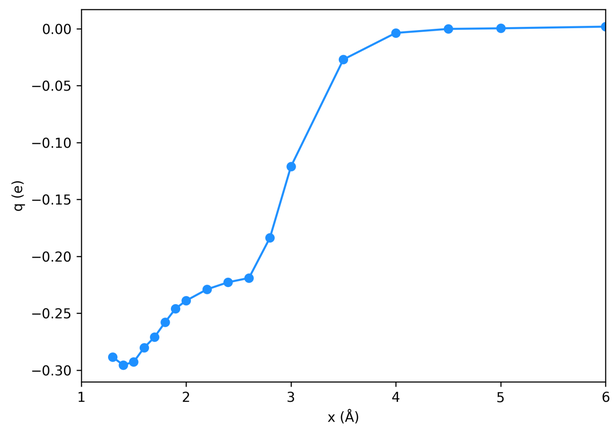
The theory was formulated by Bader and provides a quantum mechanical justification of the concept of atoms. Atomic basins are regions delimitated by zero-flux surfaces, where the directional derivative of the charge density along the surface normal ***n(r)*** is zero.

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$$

The atomic charge is obtained by integrating the electron density over the atomic basin Ω_H:

$$q_H = Z_H - \int_{\Omega_H} \rho(\mathbf{r})d\mathbf{r}$$





The Bader charge was calculated for a H atom at different distances from a Ge(111) surface in the adiabatic setup.
The hydrogen partially gains electrons as it approaches the surface.

5. Application in quantum-classical dynamics [2]

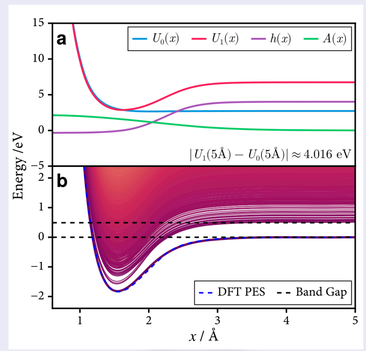
Electronic Hamiltonian in second quantization:

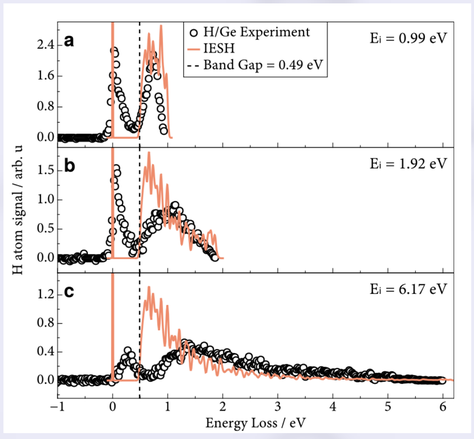
$$\hat{H}_{el}(x) = h(x)\hat{d}^\dagger\hat{d} + \sum_{k=1}^{N}\epsilon_k\hat{c}_k^\dagger\hat{c}_k + \sum_{k=1}^{N}V_k(x)(\hat{d}^\dagger\hat{c}_k + \hat{c}_k^\dagger\hat{d})$$

$$h(x) = U_1(x) - U_0(x)$$

H- anionic H neutral

Independent Electron Surface Hopping (IESH) calculates the hopping probability between electronic states and propagates the dynamics accordingly.





[2] L. Xuexun *et al.* J. Chem. Phys. **2026** 164, 024707