UNIVERSITÄT DUISBURG ESSEN

SFB 616

Perturbative approach for e-h-pair excitations in adsorption

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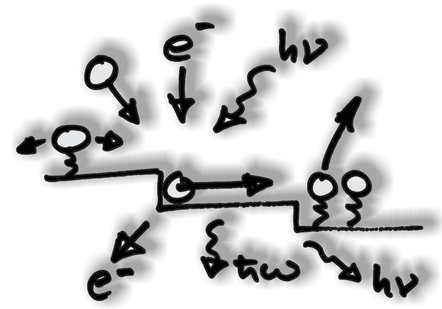

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Goals

- Non-adiabatic effects in adsorption on metal surfaces: Calculate the excitation spectrum of electrons and holes
- Develop a method that is more flexible and/or faster than previous methods (TDDFT, electronic friction, Newns-Anderson model)
- Explain the isotope effect in chemicurrent experiments
- Is it necessary to include nonadiabatic effects regarding the spin relaxation?

Experimental setup

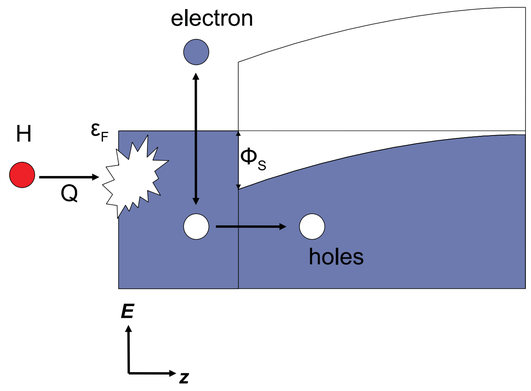
I. Schottky diode with Fermi energy ε_F and Schottky barrier height ϕ_S, consisting of a metal surface on a (usually) p-doped semiconductor

II. Atom approaches surface perpendicularly (reaction coordinate Q)

III. Excitation of electrons and holes

IV. Holes (or electrons) can pass the Schottky barrier if their energy is large enough

V. Measurement of a (chemi-)current between metal and semiconductor



Theoretical Approach

Perturbation theory

Hamiltonian [1]

$$H_F(t) = \sum_{k,\sigma} \varepsilon_{k,\sigma} \psi^\dagger_{k,\sigma} \psi_{k,\sigma} + \sum_{k_1,k_2,\sigma} V_{k_1,k_2,\sigma}(t) \psi^\dagger_{k_1,\sigma} \psi_{k_2,\sigma} = H_0 + V(t)$$

- ε_k energy of electrons
- $\psi^\dagger_k / \psi_k$ creator/annihilator of electron
- $V_{k_1,k_2,\sigma}(t)$ matrix elements of perturbation
- σ spin ($\uparrow$ or $\downarrow$)

Perturbative aproach

- perturbation rapid and small
- first-order perturbation theory sufficient
- can use unperturbed electronic eigenstates

Difference to previous approaches

- no nonadiabatic wavefunctions / potential (in contrast to TDDFT [2,3])
- can calculate electronic spectrum (in contrast to electronic friction [4])
- direct DFT approach (in contrast to Newns-Anderson model [5])

Spectrum

Matrix elements of perturbation

$$\lambda_{ij} = \int dt \left\langle \varepsilon_i \left| \frac{\partial V}{\partial Q} \right| \varepsilon_j \right\rangle \frac{dQ}{dt} \exp(i(\varepsilon_j - \varepsilon_i)t/\hbar)$$

- $|\varepsilon_j\rangle$ unperturbed electronic eigenstates
- V effective potential
- Q reaction coordinate

Spectrum of electron-hole pairs

$$P_{\mathrm{ex,eh}}(\omega) = \frac{1}{\hbar^2} \sum_{ij} \left| \frac{\lambda_{ij}}{\varepsilon_j - \varepsilon_i} \right|^2 (f(\varepsilon_j) - f(\varepsilon_i))\, \delta(\omega - (\varepsilon_j - \varepsilon_i))\, \theta(\omega)$$

- $f(\varepsilon)$ occupation function (temperature dependent)
- takes into account de-excitation effect

Spectrum of electrons (and holes)

$$P_{\mathrm{ex,el}}(\omega) = \frac{1}{\hbar^2} \sum_{ij} \left| \frac{\lambda_{ij}}{\varepsilon_j - \varepsilon_i} \right|^2 (f(\varepsilon_j) - f(\varepsilon_i))\, \delta(\omega - (\varepsilon_j - \varepsilon_F))\, \theta(\omega)$$

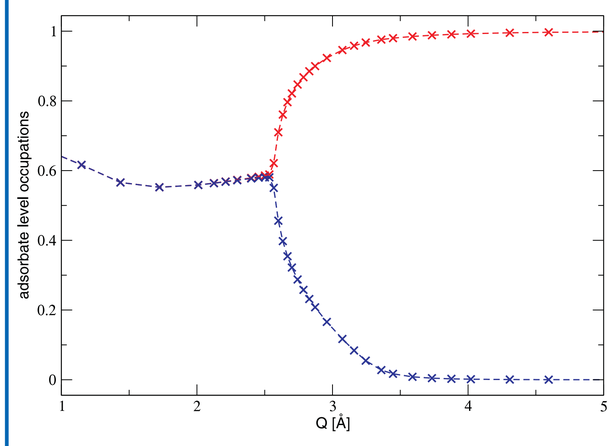
- ε_F Fermi-energy

Energy dissipation

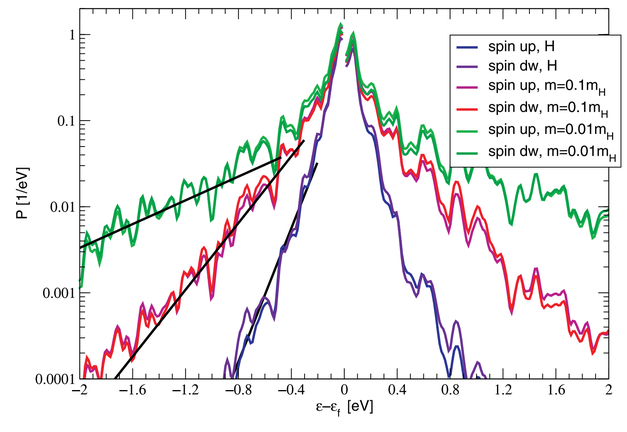
$$E_{diss} = \int d\omega\, \omega P_{ex,eh}(\omega)$$

Results

Spin transition

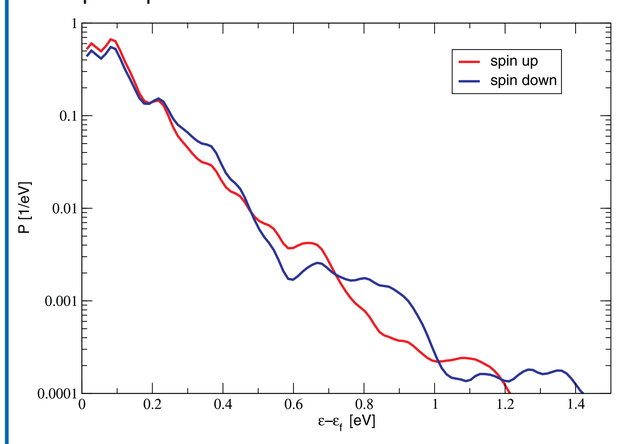


Electron and hole spectra: isotope effect

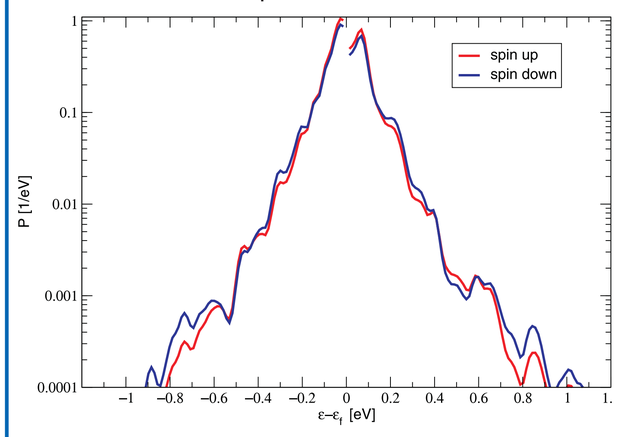


Spectra

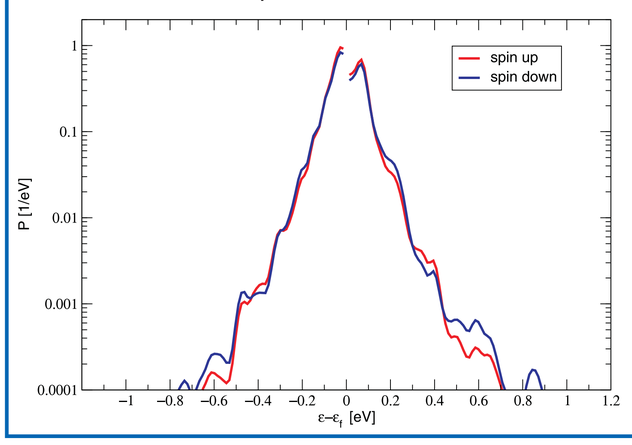
e-h pair spectrum: H



Electron and hole spectrum: H

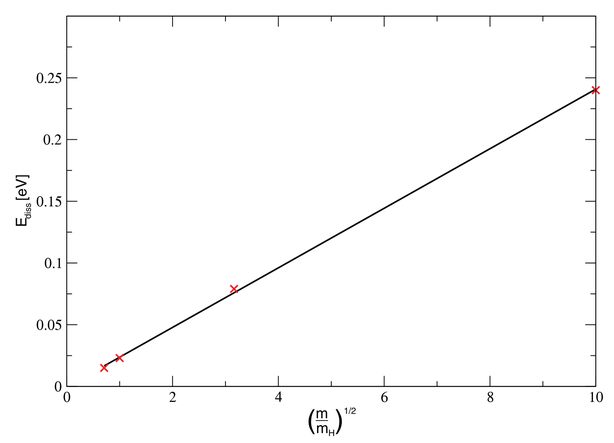


Electron and hole spectrum: D

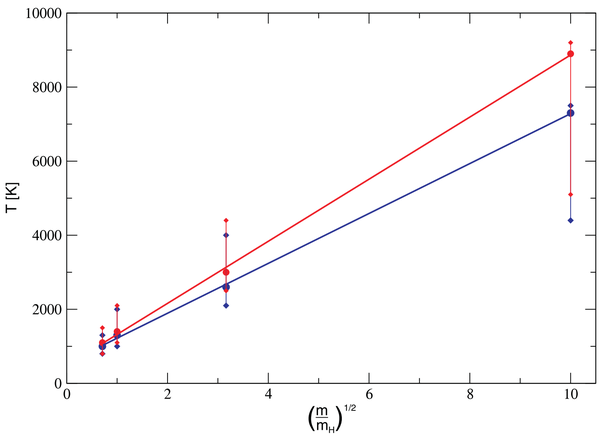


Scaled mass behavior

Dissipated energy vs. scaled mass



Fitted temperature vs. scaled mass



Particles passsing the Schottky barrier (0.48 eV)

Isotope	Electrons	Holes
Deuterium	0.000246	0.000175
Hydrogen	0.000781	0.000561
N/N_D	3.17	3.21
$N/N_{D,Experiment}$		3.7 ± 0.7 [6]
H: m = 0.1 m_H	0.021502	0.014713
N/N_H	27.53	26.23
H: m = 0.01 m_H	0.088775	0.064376
N/N_H	113.67	114.75

DFT Calculations

Calculational details

System

H above Al-(111) on-top position

12 layers of Al

$2\sqrt{3} \times 2\sqrt{3}$ unit cell

Quantum-Espresso code

4 x 4 x 1 Monkhorst-Pack k-point grid

21 Ry cutoff energy

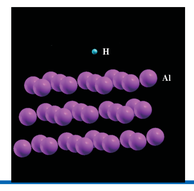
GGA PBE nc pseudotentials

Dynamics

35 different positions of the H atom

classical dynamics for movement of H atom

one half round trip

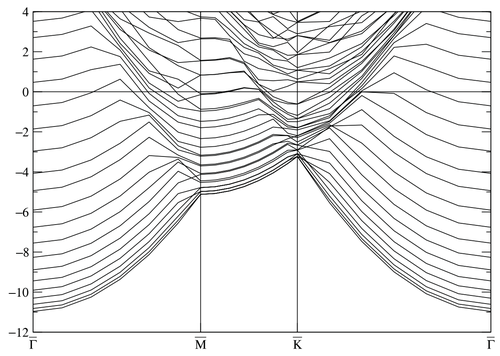


Sketch of our system: Hydrogen on the on-top position of an Al-111 surface

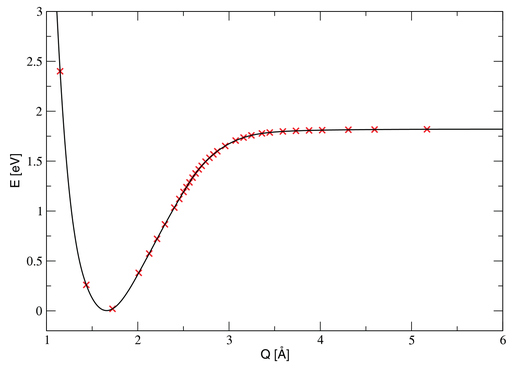
Results

Al lattice constant: 4.06 Å

Surface band structure



Potential energy



Discussion

Achievements

- DFT approach
- New method for calculation of spectra and energy loss due to electronic excitations
- Method is computationally fast, and can be implemented in existing codes (post-processing)
- It is formally not necessary to include spin relaxation effects (no divergences)
- Unlinke in the friction picture there are excitations with a finite energy
- Spin effects are within the error bar
- We can explain the isotope effect
- Scaled mass behavior

Future Goals

- Further investigation of spin effect
- Molecular adsorption
- Other systems

Acknowledgements

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Literature

1) E. Müller-Hartmann, T.V. Ramakrishnan, G. Toulouse, Phys. Rev. B **3**, 1102 (1971)
2) M. Lindenblatt, J. van Heys, E. Pehlke, Surf. Sci. **600**, 3624 (2006)
3) M. Lindenblatt, E. Pehlke, Phys. Rev. Lett. **97**, 216101 (2006)
4) J.R. Trail, M.C. Graham, D.M. Bird, M. Persson, S. Holloway, Phys. Rev. Lett. **88**, 166802 (2002)
5) M.S. Mizielinski, D.M. Bird, M. Persson, S. Holloway, J. Chem. Phys. **126**, 034705 (2007)
6) H. Nienhaus, D. Krix, S. Glass, J. Vac. Sci. Technol. A **25**, 950 (2007)