General calculation scheme

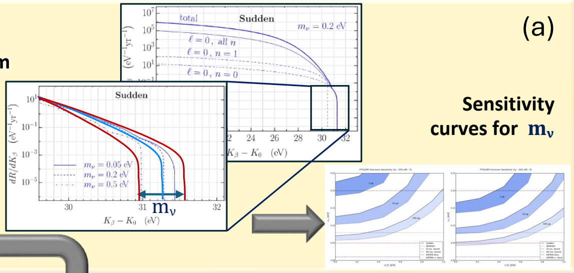
$\mathrm{T@gr} \rightarrow e^- + \bar{\nu} + {}^3\mathrm{He}^*\mathrm{@gr}$ (a)

- Calculation of the **β electron energy spectrum**

$$M_f = \frac{g}{V}\int \psi_{i,\mathrm{T}}\psi^*_{f\,He}\, e^{-i(p_e+p_\nu)\cdot x}$$

- ✓ The shape of the spectrum at its endpoint reveals the ν mass…
- ✓ … but depends on T and He potentials

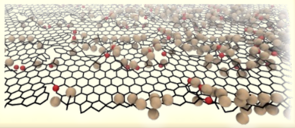
$$\Delta K \sim \Delta U_0 + \frac{1}{2}\hbar(\omega_T^{\perp} - \omega_{He}^{\perp}) + \hbar(\omega_T^{\parallel} - \omega_{He}^{\parallel})$$

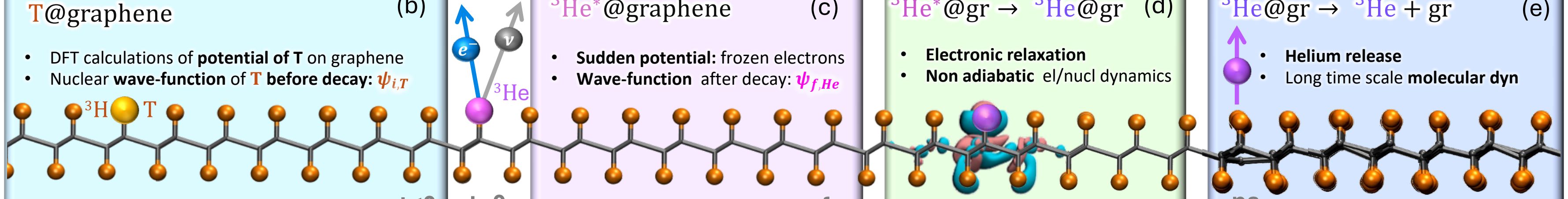


Sensitivity curves for $\mathbf{m_\nu}$

Long time scale effects (f)

- ✓ Substrate heating up, consumption, degradation
- ✓ Possible signals from the substrate

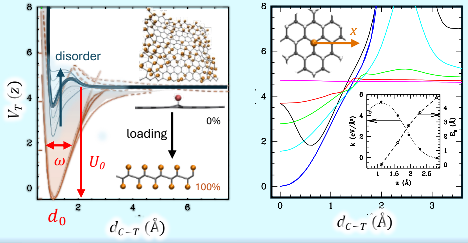




T@graphene (b)

- DFT calculations of **potential of T** on graphene
- Nuclear **wave-function** of **T before decay:** $\psi_{i,T}$

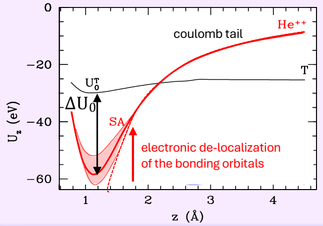
- ✓ **Dependence** of the T potential and of $\psi_{i,T}$ on the **level and distribution of loading**



${}^3\mathrm{He}^*$@graphene (c)

- **Sudden potential:** frozen electrons
- **Wave-function** after decay: $\psi_{f,He}$

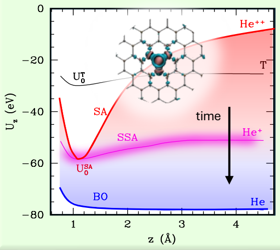
- ✓ **Dependence** of the sudden potential and of $\psi_{f,He}$ on the local **electronic structure** (and on load/distribution)



${}^3\mathrm{He}^*\mathrm{@gr} \rightarrow {}^3\mathrm{He@gr}$ (d)

- **Electronic relaxation**
- **Non adiabatic** el/nucl dynamics

- ✓ Evolution of He potential
- ✓ **Final charge state** of He

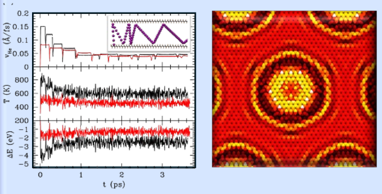


${}^3\mathrm{He@gr} \rightarrow {}^3\mathrm{He} + \mathrm{gr}$ (e)

- **Helium release**
- Long time scale **molecular dyn**

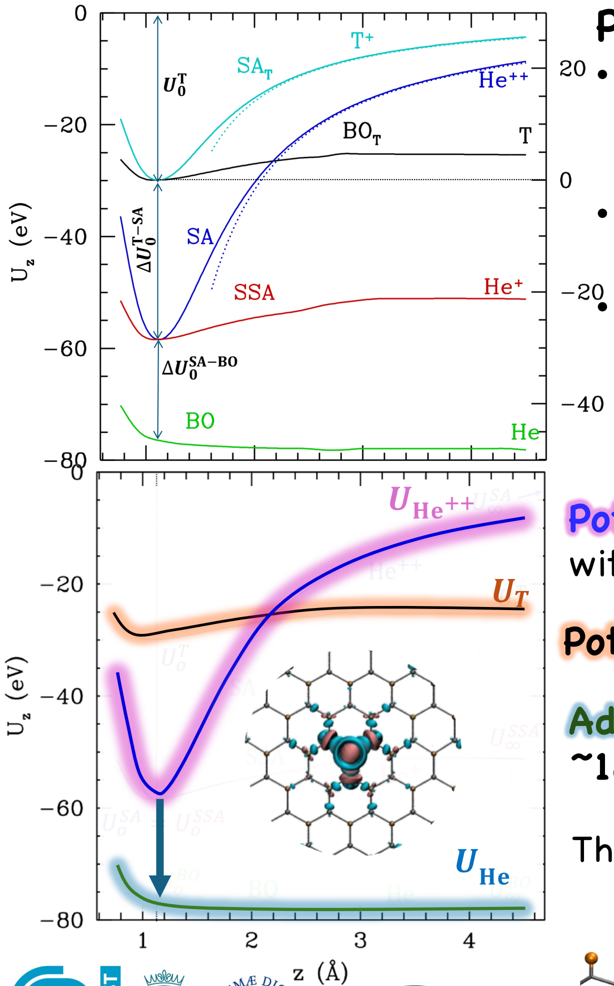
The post-reaction molecular dynamics

- ✓ Recoil and He secondary interactions
- ✓ Vibrational modes/flexural phonons
- ✓ El excitations, charge/spin dens waves



Combined quantum treatment of nuclei with ab initio electronic calculations

$$M \sim \int d\mathbf{x}\, \Psi_0^T \Psi_f^{*\mathrm{He}} e^{i(p_{el}+p_\nu)\cdot \mathbf{x}}$$



Potentials alignment:

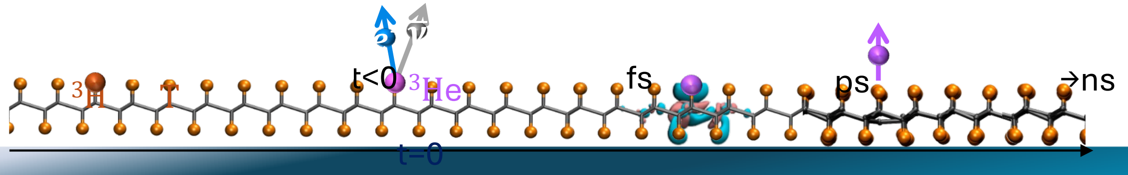
- The **blue**, **red** and **green** lines are all potentials for He though in different charge states. The systems have same composition and DFT gives directly the relative alighments
- The cyan and **black** lines are all potential for T, and for the same reason the relative alignment is given by DFT calculation
- The relative alignment between the block blue/red/green and black/cyan is not correctly given by DFT; however sudden approx for He and for T release naked He++ and T+ nuclei, while all the rest of the system is frozen. Therefore they have a common 0 reference at infinity

Potential of He just after the nuclear reaction: sudden approximation obtained with **frozen electrons.** Binding energy ~50 eV, and He exit in ionic form

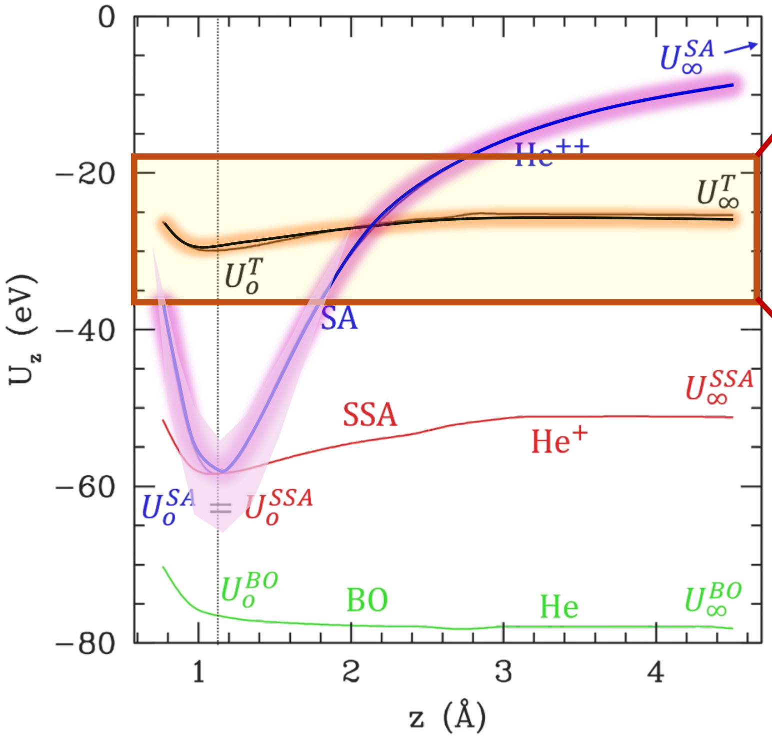
Potential for T obtained within BO-DFT approximation. Binding energy ~4.5 eV

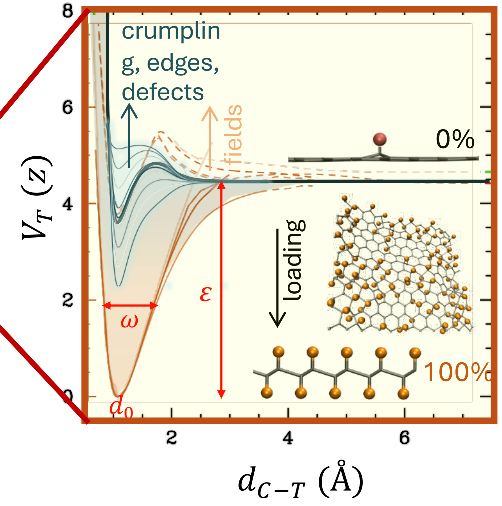
Adiabatic potential for He. Electronic structure is relaxed
~18 eV energy decrease

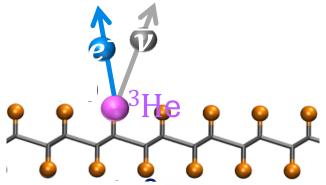
The potential becomes **repulsive** and He is subsequently released in neutral form

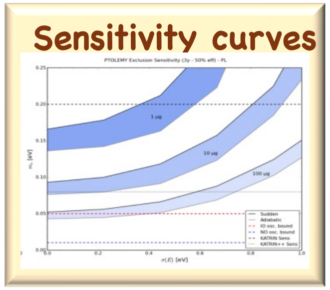


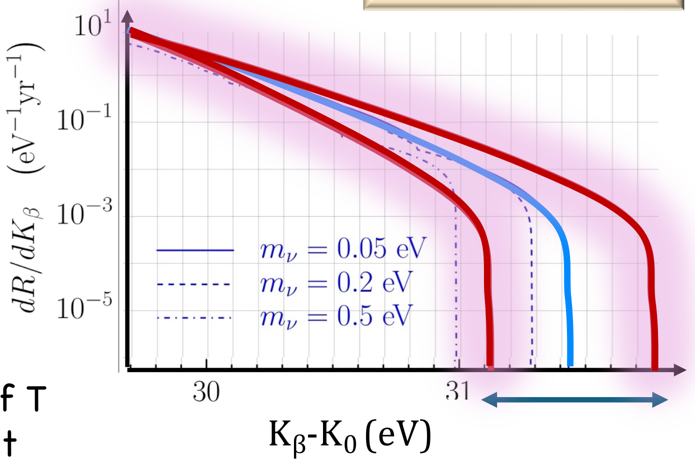
All potentials depend on the loading and distribution of T on graphene





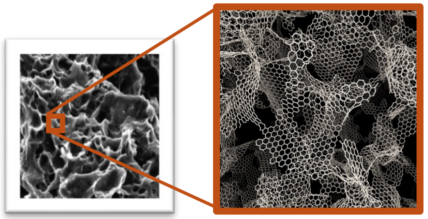


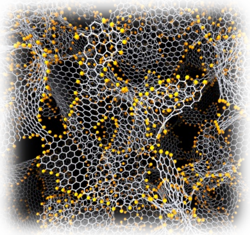

Sensitivity curves

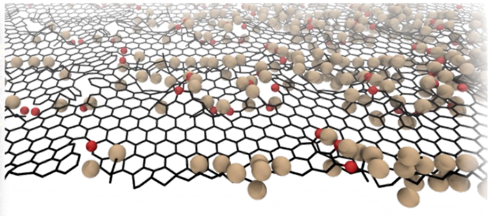


Different loading/distribution of T change the potential and affect spectra and sensitivity

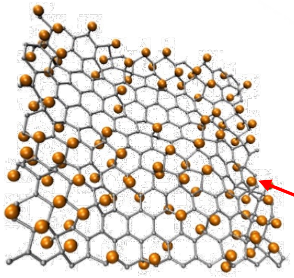
$$K_\beta^{end} = Q - m_\upsilon + (U_o^T - U_o^{He}) + \frac{1}{2}\hbar(\omega^T - \omega^{He})$$







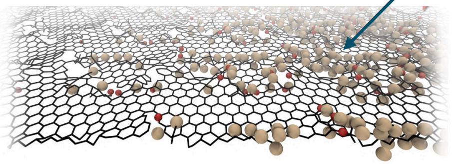
Binding energy of T: depends on the loading level, local distribution of T (above and below)

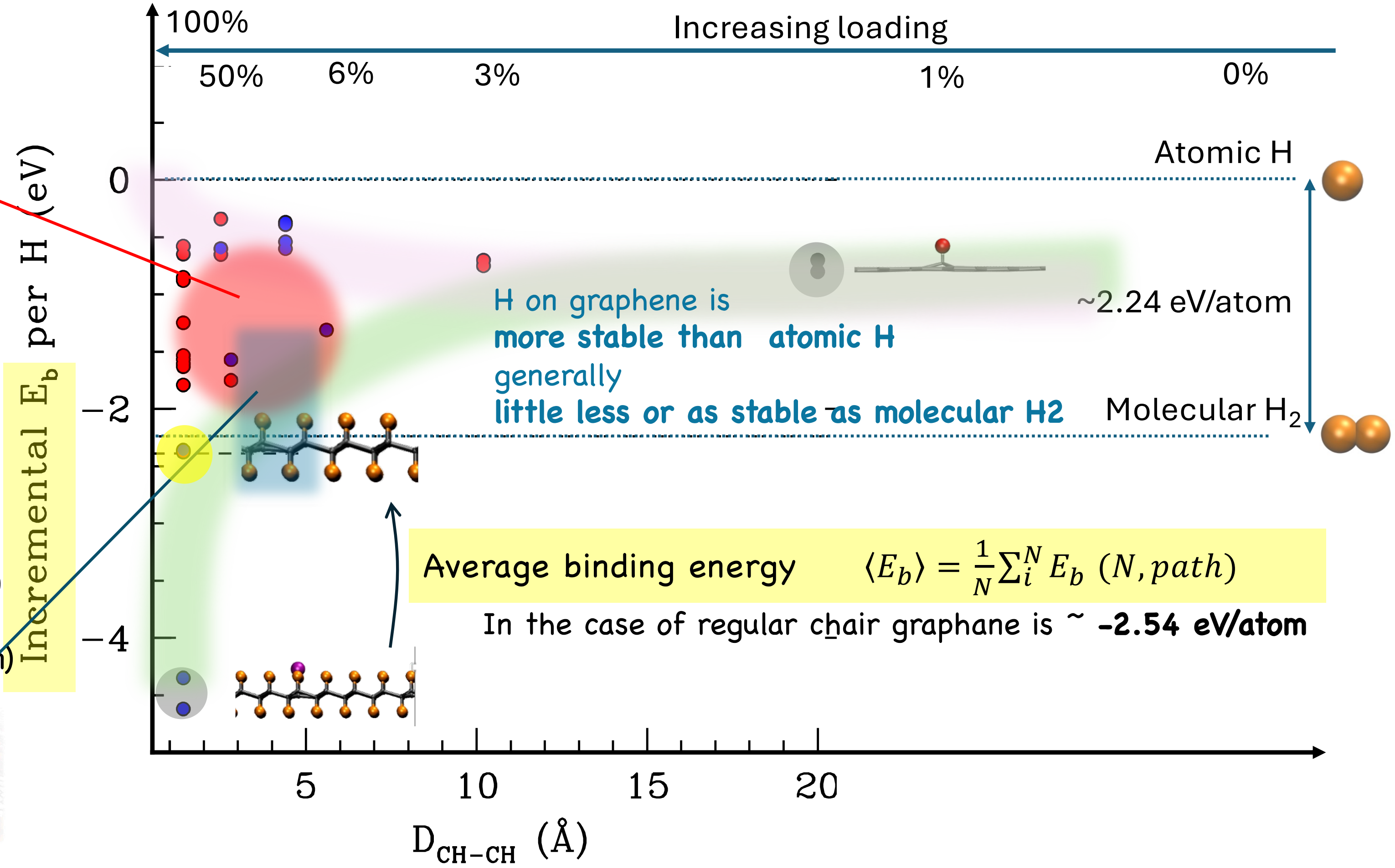


In the case of **random hydrogenation**, the Average Binding energy depends is located approximately here.

Stability of hydrogenated graphene depends on

- **Loading level**
- **defects** (especially **edges**)
- Presence of **other elements** (typically **oxygen**)





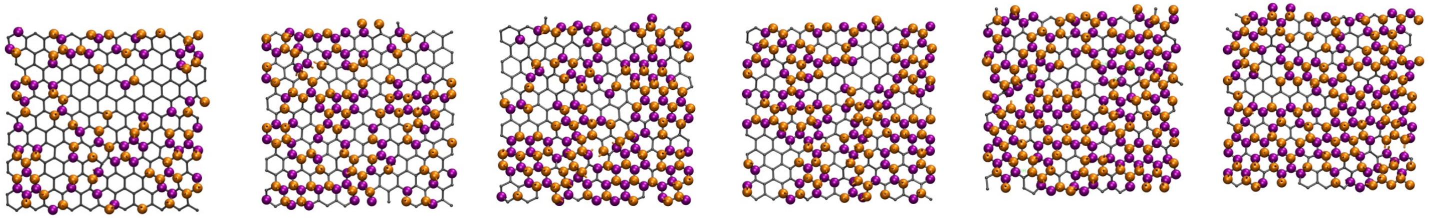
H on graphene is **more stable than atomic H** generally **little less or as stable as molecular H2**

Average binding energy $\langle E_b \rangle = \frac{1}{N}\sum_i^N E_b\ (N, path)$

In the case of regular chair graphane is ~ **-2.54 eV/atom**

Classical MD with reactive FF (2024) + DFT Data (2022-2025)

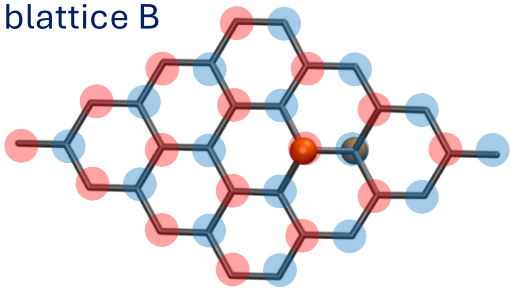
From Delfino et al 2024: structures are obtained exposing the sheets to atomic H at high temperature (details in the paper)

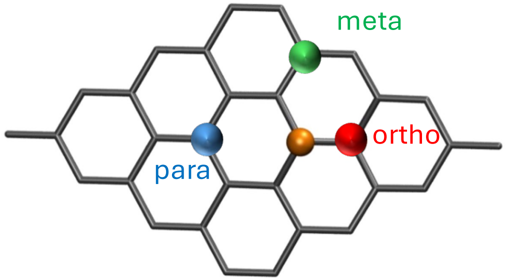


Cov %	41	54	66	63	78	76
Tot orto	55,80	48,90	61,49	49,99	58,45	50,97
Tot met	17,40	14,27	18,06	15,51	17,55	14,15
Tot para	5,97	4,89	5,16	4,75	4,86	6,09
uu orto	33,00	32,10	39,70	50,29	45,23	42,12
uu met	20,00	20,03	24,63	23,29	16,73	22,96
uu para	7,98	3,87	5,43	4,70	2,96	4,54
dd orto	63,94	30,35	45,71	31,67	41,29	33,59
dd met	21,51	23,60	29,07	20,31	15,47	21,17
dd para	5,37	3,78	4,19	4,10	5,39	5,06
ud orto	64,10	69,10	80,00	58,37	77,89	63,70
ud met	28,30	15,40	20,57	26,38	21,10	19,21
ud para	9,47	6,71	8,33	5,53	7,58	7,93
uu_orto_normal	0,59	0,66	0,65	1,01	0,77	0,83
uu_m_norm	1,15	1,40	1,36	1,50	0,95	1,62
uu_para_norm	1,34	0,79	1,05	0,99	0,61	0,75
dd_o_norm	1,15	0,62	0,74	0,63	0,71	0,66
dd_met_norm	1,24	1,65	1,61	1,31	0,88	1,50
dd_para_norm	0,90	0,77	0,81	0,86	1,11	0,83
ud_o_norm	1,15	1,41	1,30	1,17	1,33	1,25
ud_m_norm	1,63	1,08	1,14	1,70	1,20	1,36
ud_p_norm	1,59	1,37	1,61	1,16	1,56	1,30

The preferred hydrogenation configuration are:
same-side meta (i.e. same sublattices)
different-side ortho (same sublattice)

This configuration also tend to maintain a low global curvature
Prehexistent curvature influence the stability and distribution





Our data (published or newly produced) allow to build a lattice model for hydrogenation

Generalized spin 1 Blume Capel-type model on honeycomb lattice 7 parameters

Simone Ritarossi, Michele Campisi, Francesco Caravelli

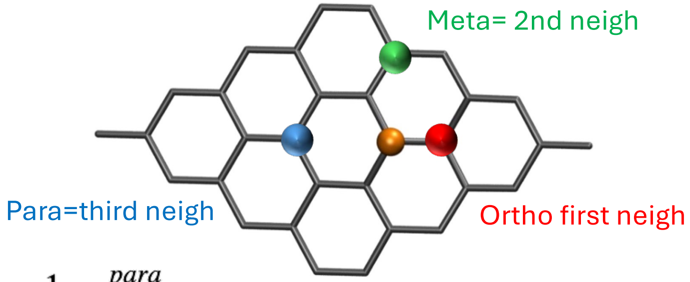
$H = \sum_{i,j} J_{ij}\,\phi_i\phi_j + \sum_i\ C_i\,\phi_i$

With:

ϕ_i = **site occupancy**, 0 = empty, +1 = occupied above -1 occupied below

J_{ij} = **incremental binding energy**, first, second and third neighbour

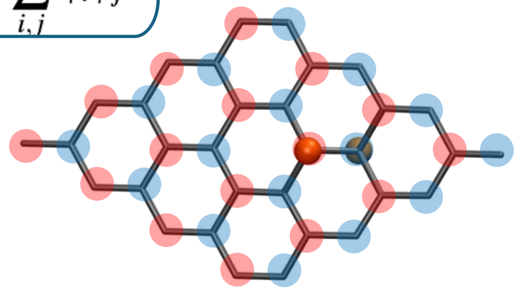
C_i = external field and or **local curvature** (to be added if needed)



$$H = -\varepsilon^0 \sum_i |\phi_i| \longrightarrow \text{Isolated T binding energy}$$

$$\underbrace{-\frac{1}{2}\Delta\varepsilon^O \sum_{i,j}^{ortho} |\phi_i\phi_j| - \frac{1}{2}\Delta\varepsilon^M \sum_{i,j}^{meta} |\phi_i\phi_j| - \frac{1}{2}\Delta\varepsilon^P \sum_{i,j}^{para} |\phi_i\phi_j| + \frac{1}{2}J^O \sum_{i,j}^{ortho} \phi_i\phi_j + \frac{1}{2}J^M \sum_{i,j}^{meta} \phi_i\phi_j + \frac{1}{2}J^P \sum_{i,j}^{para} \phi_i\phi_j}_{\text{neighbors interactions}}$$

$$+MF(|\phi|)\sum_i \phi_i + \sum_i C_i\phi_i \longrightarrow \text{External fields/curvature}$$



Sublattice A

Sublattice B

OR: (change notation $|\phi_i| \to \rho_i$ and $\phi_i \to \sigma_i$, and add chemical potential)

$$\mathcal{H} = -\sum_{k=1}^{3} J_\rho^{(k)} \sum_{\langle ij\rangle_k} \rho_i\rho_j - \sum_{k=1}^{3} J_\sigma^{(k)} \sum_{\langle ij\rangle_k} \sigma_i\sigma_j + (\mu - \varepsilon_0)\sum_i \rho_i$$

Our data (published or newly produced) allow to build a lattice model for hydrogenation

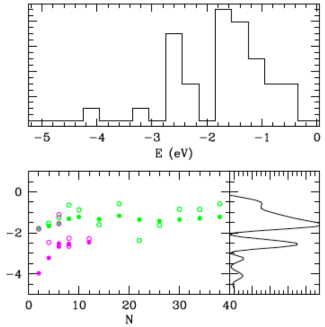
The parameterization of the fixed terms (binding energies and interaction energies) is available,

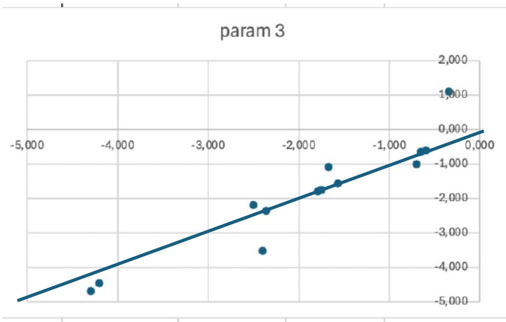
and benchmarked over a number of known configurations

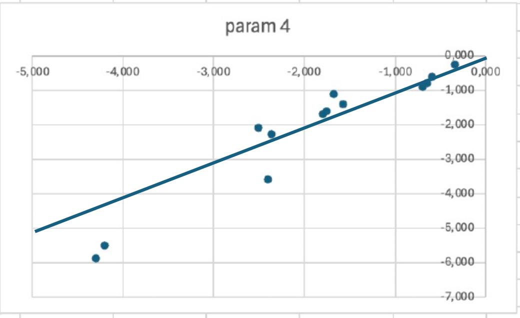
though it can be improved with more data

configuration	n^O	n^M	n^P	Φ^O	Φ^M	Φ^P	E_b (eV)	E_b range	$\langle E\rangle/N$ (eV)	Param 3	Param 4
isolated	0	0	0	0	0	0	-1.0	-0.7,-1.3	same	-1.000	-0.900
chair	3	6	3	-3	+6	-3	-4.5	-4.3,-5.2	-2.39	-4.690	-5.865
chair one side	0	6	0	0	+6	0	-0.34	??		+1.100	-0.240
boat	3	6	3	-1	-2	+3	-4.3	$\sim chair + 0.12$	-2.33	-4.460	-5.505
all one side	3	6	3	+3	+6	+3	-2.4	-1.6 , -2.8	-1.6,-2.4	-3.520	-3.585
tetra	1	2	0	+1	+2	0	-1.67	-1.4 , -3.2		-1.090	-1.095
6H	1	1	1	+1	+1	+1	-2.5	-2.7 , -2.1		-2.190	-2.085
ortho trans	1	0	0	-1	0	0	-2.36	-2.6, -2		-2.360	-2.275
ortho cis	1	0	0	+1	0	0	-1.79	-2, -1.5		-1.790	-1.675
meta trans	0	1	0	0	-1	0	-0.60	-0.9,0.5		-0.600	-0.610
meta cis	0	1	0	0	+1	0	-0.65	-0.9,0.5		-0.650	-0.790
para trans	0	0	1	0	0	-1	-1.57	-1.9,1.4		-1.570	-1.400
para cis	0	0	1	0	0	+1	-1.75	-2,1.6		-1.750	-1.600
parameters	ε_0			$\Delta\varepsilon^O$	$\Delta\varepsilon^M$	$\Delta\varepsilon^P$	J^O	J^M	J^P		
Param 3	-1.0			1.075	-0.375	0.66	0.285	-0.025	-0.09		
Param 4	-0.9			1.075	-0.20	0.6	0.3	-0.09	-0.1		

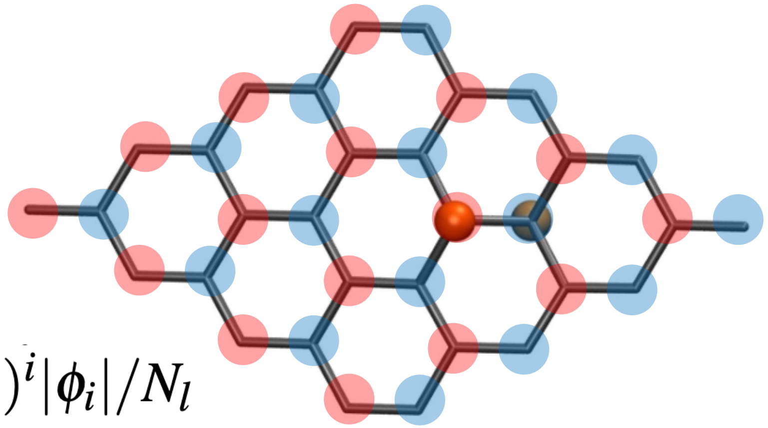
NB: the most stable configuration is that with alternated occupation above and below (staggered), called the chair conformation







Preliminary results of Monte Carlo Simulations


Sublattice A
Sublattice B

Order parameters

Average occupation $\langle|\phi_i|\rangle = \langle\phi_i^2\rangle$

Average "magnetization" $m = \langle\phi_i\rangle$

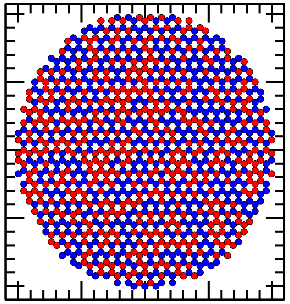
Average staggered occupation $n^s = \langle n_{i_A}\rangle - \langle n_{i_B}\rangle = \sum_i(-1)^i|\phi_i|/N_l$

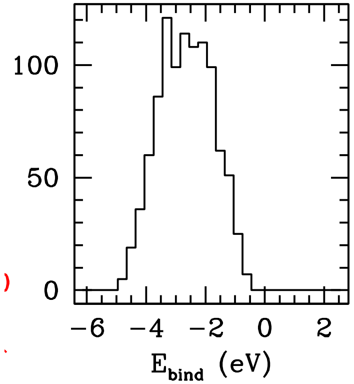
Average staggered "magnetization" $m^s = \langle\phi_{i_A}\rangle - \langle\phi_{i_B}\rangle = \sum_i(-1)^i\phi_i/N_l$

The phase diagram is studied in the plane T-μ (temperature chemical potenitial/fugacity, which in turn depends on the gas external concentration of tritium

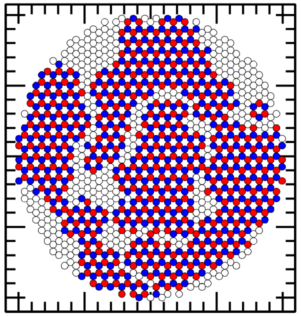
$$\mathcal{H} = -\sum_{k=1}^{3} J_\rho^{(k)} \sum_{\langle ij\rangle_k} \rho_i\rho_j - \sum_{k=1}^{3} J_\sigma^{(k)} \sum_{\langle ij\rangle_k} \sigma_i\sigma_j + (\mu - \varepsilon_0)\sum_i \rho_i$$

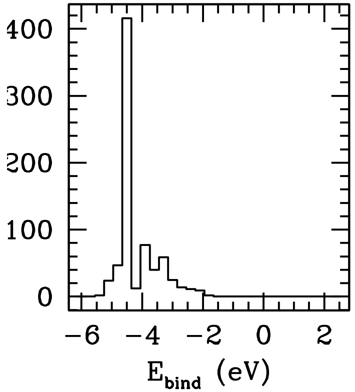
Preliminary results of Monte Carlo Simulations (small system, dyn and energy distrib)



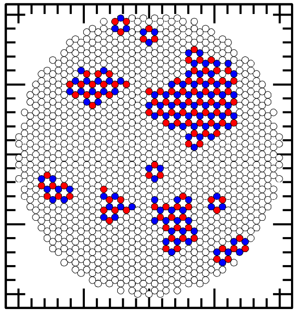


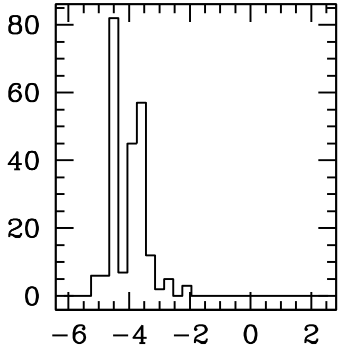
T=2000, μ=0
n=1
m = small
ns= small
ms=0.2



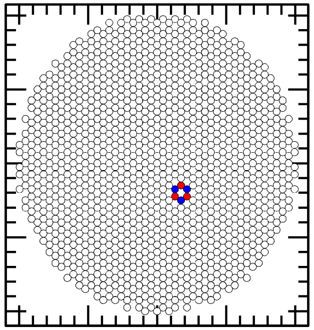


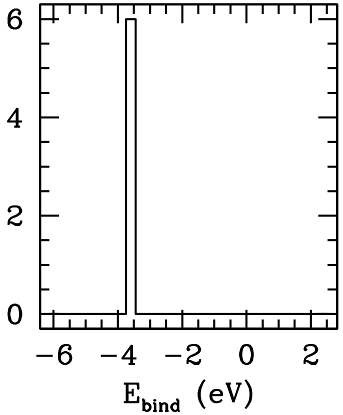
T=2000, μ=2.3
n=0.8
m = small
ns= small
ms=0.7





T=2000, μ=2.4
n=0.5
m = small
ns= small
ms=0.5





T=2000, μ=2.5
n=0.01
m = small
ns= small
ms=0.01

Preliminary results of Monte Carlo Simulations +MF (Simone)

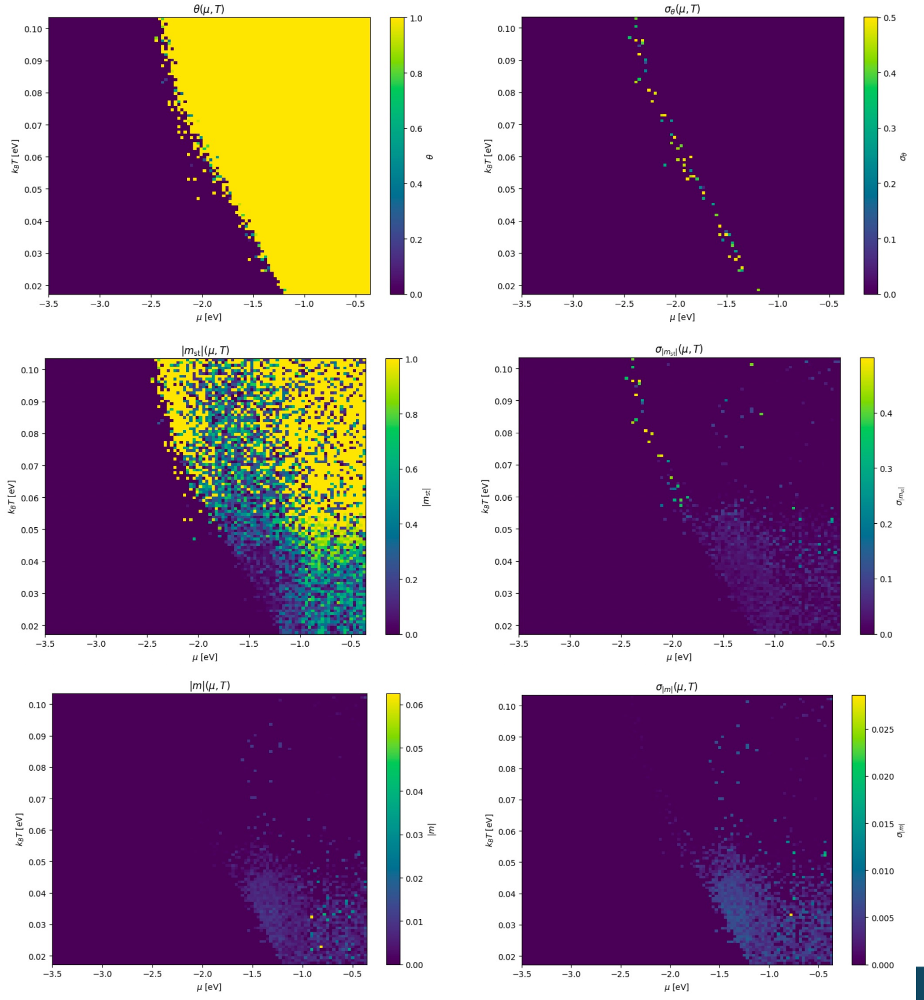
MC

Variance

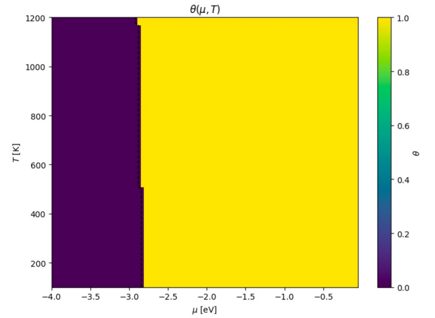
n occupancy

Staggered magn ms

magnetz

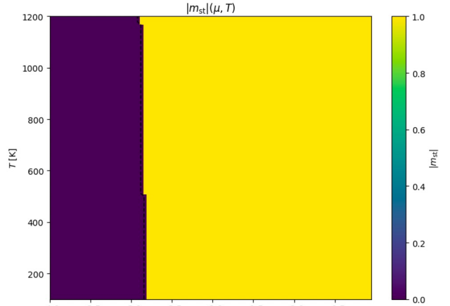


Mean field (large T)



Occupancy is stabilized at high temperature and low (absolute) fugacity

Staggered magnetization (i.e. alternate occupation) is preferred as the temperature increases



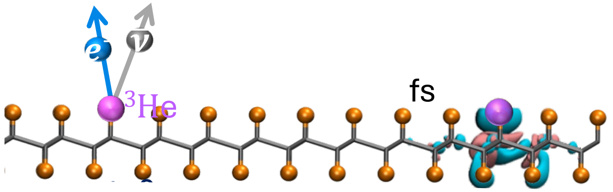
Same side occupation can be weakly stabilized at Low temperature and high chem potential

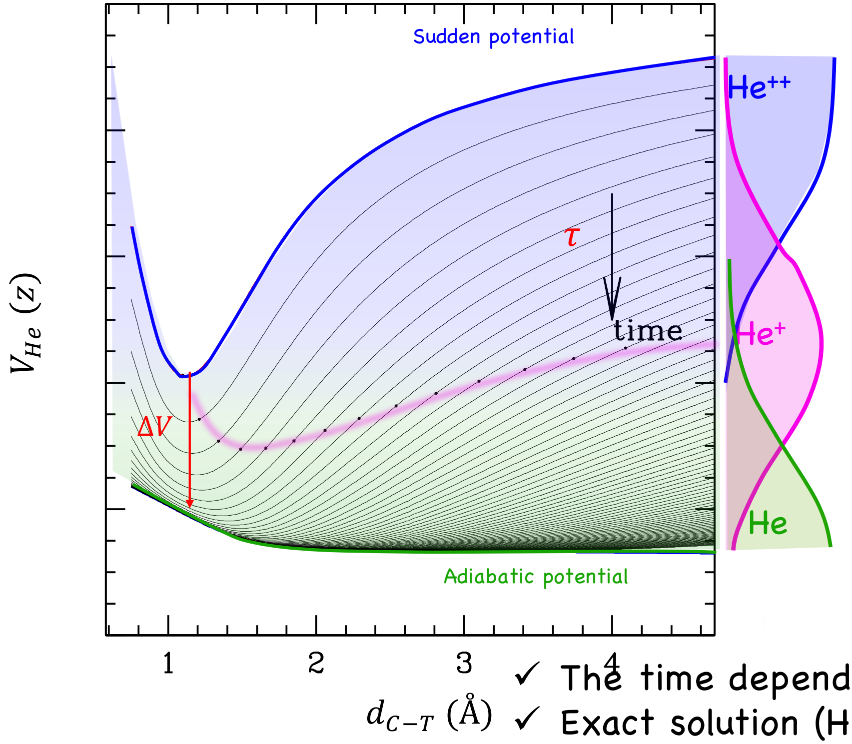
- ✓ An analytic study (in mean field approx) is currently in the course
- ✓ We are evaluating the possibility of implementing the mode in a quantum annealer

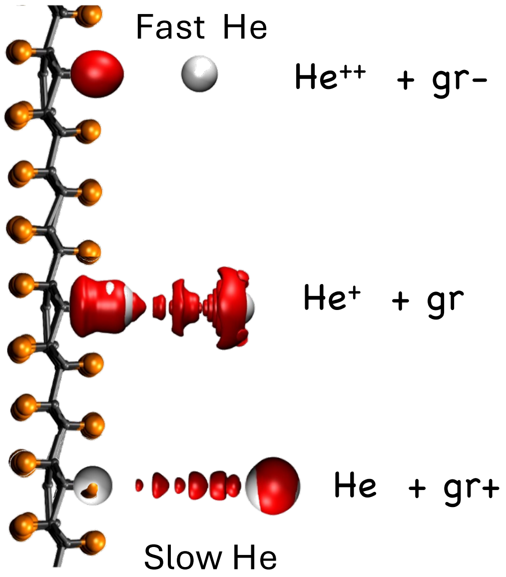
The non adiabatic dynamics

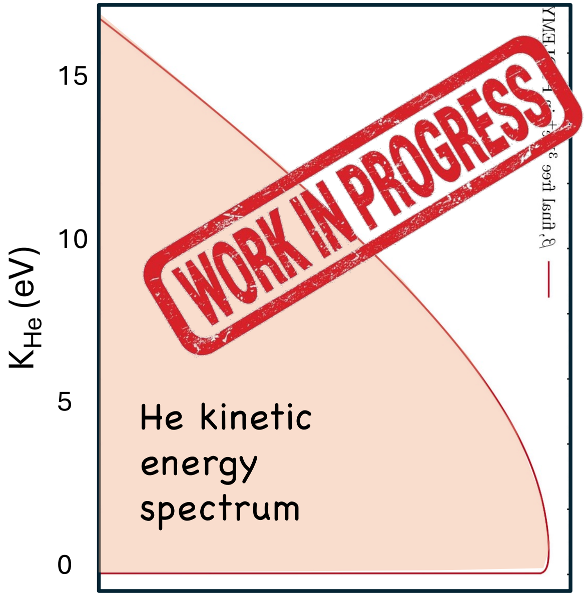
As electronic structure relaxes, the potential changes from the **sudden to the adiabatic**

→ **He feels a non adiabatic time dependent potential**







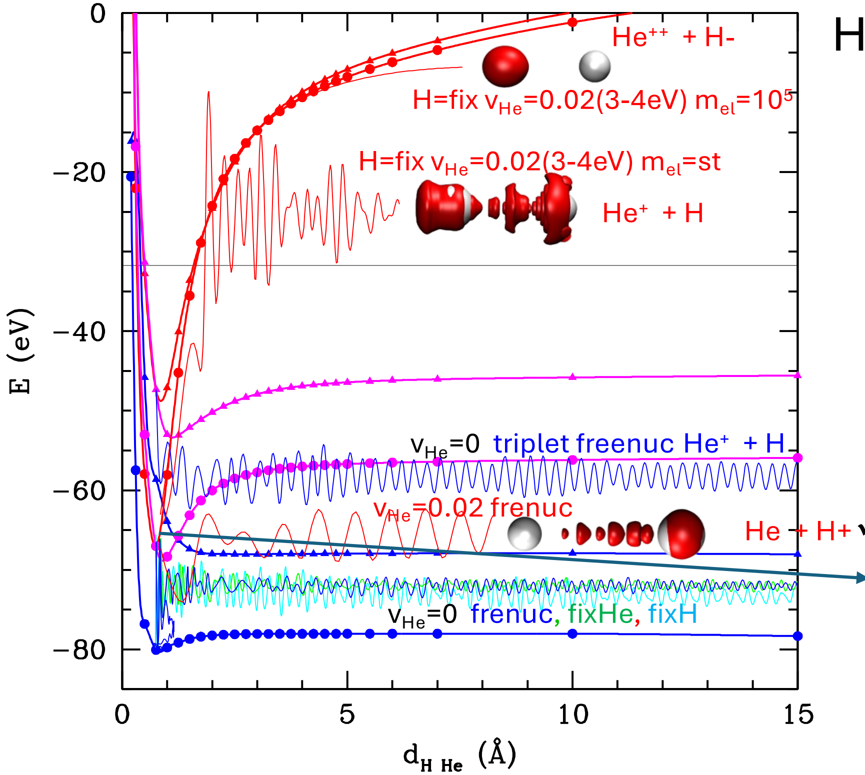


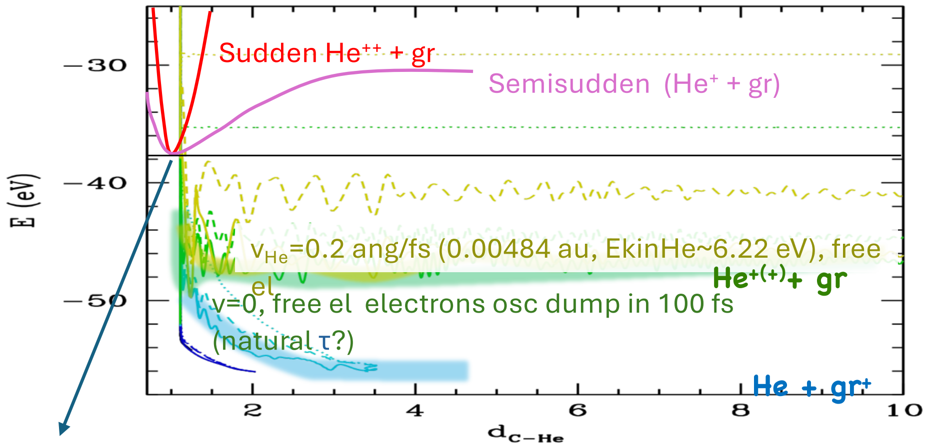
- ✓ The time dependent Schroedinger eq for electrons must be solved a nuclei move
- ✓ Exact solution (Herhenfest dynamics) is in the course (Carlo Andrea Rozzi)
- ✓ "Quick and dirty" gives different ionic states depending on its energy after decay
- ✓ **Calculations on TT and HT molecules will be compared with TRIMS**

The non adiabatic dynamics. (Carlo Andrea Rozzi, NANO-CNR)

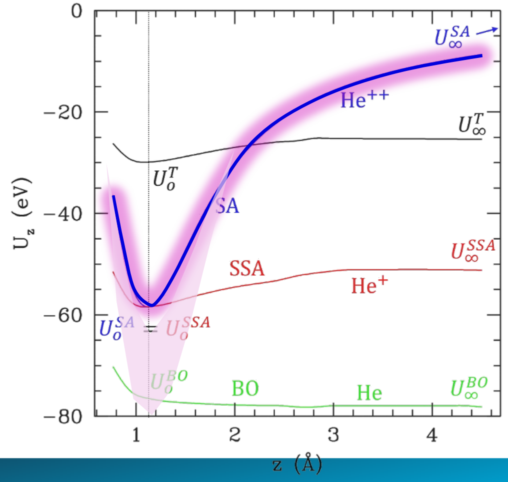
T@graphene

H-T





- ✓ The energy of He after decay ALSO depends on the environment (specifically on the localization of charge before decay)



- ✓ The final charge state depends on the interplay between relaxation time and energy of He (He energy spectrum)
- ✓ The relaxation time depends on the environment (different berween HT and T@graphene and depending on loading