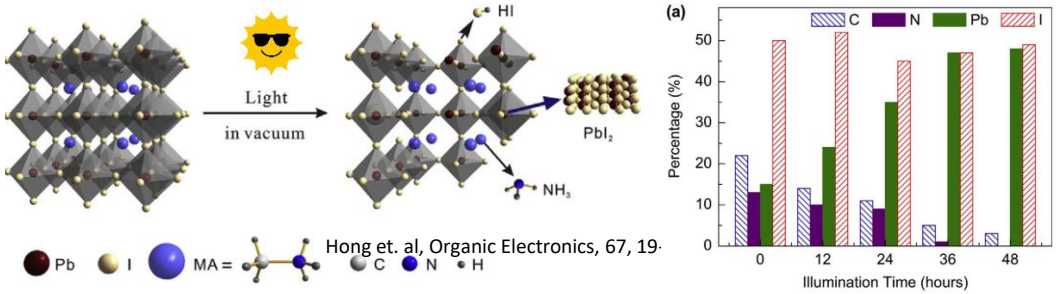
Excited-state forces in organic metal halide perovskites from GW/BSE calculations

Rafael Del Grande – rdelgrande@ucmerced.edu
David Strubbe

SAIL Strubbe Ab Initio Laboratory

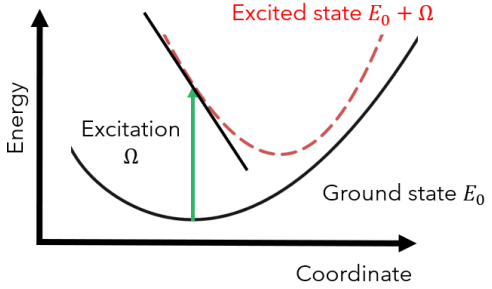
UNIVERSITY OF CALIFORNIA MERCED

Motivation - Light induced structural changes



Hong et. al, Organic Electronics, 67, 19-

Methodology - Excited state forces



$$\partial\Omega = \sum_{cvc'v'} A^*_{cv} A_{c'v'} \left(\partial H^{qp}_{cc'} - \partial H^{qp}_{vv'} + \partial K_{cvc'v'}\right)$$

Where

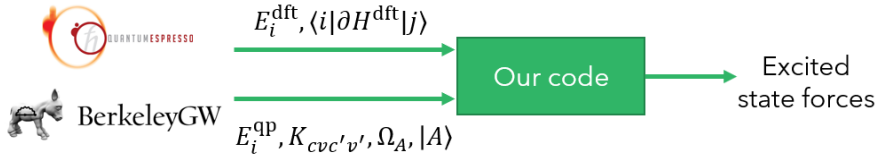
$$\partial H^{qp}_{ij} = \begin{cases} \partial H^{dft}_{ii} \text{ if } i = j \\ \partial H^{dft}_{ij} \Delta E^{qp}_{ij} / \Delta E^{dft}_{ij} \text{ if } i \neq j \end{cases}$$

And

$$\partial K_{cvc'v'} = \sum_j \partial H^{dft}_{jc} K_{cvjv'} / \Delta E^{qp(dft)}_{jc} + 3 \text{ other similar terms}$$

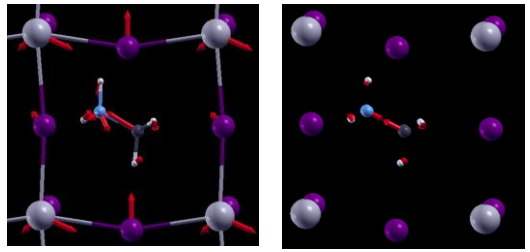
$$\partial H_{ij} = \langle i | \partial H | j \rangle \text{ and } \Delta E_{ij} = E_i - E_j$$

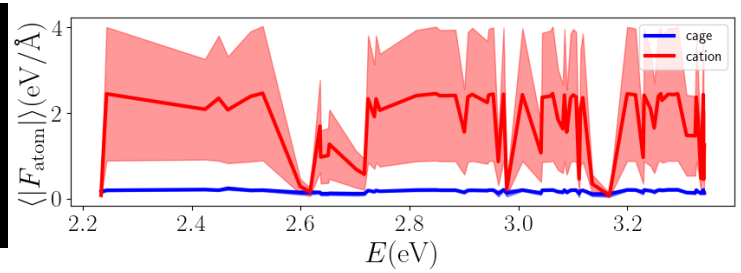
Ismail-Beigi and Louie, PRL 90, 076401 (2003)
David Strubbe Phd Thesis (2012)



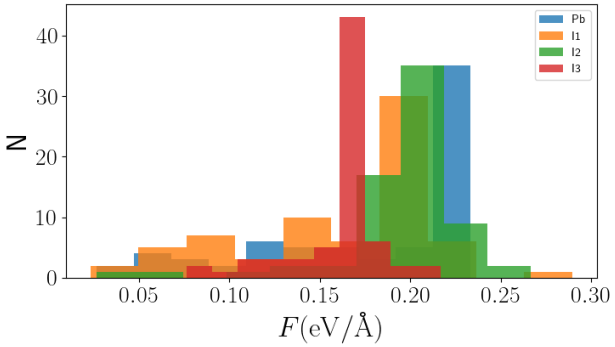
Results - Excited state forces on cubic $CH_3NH_3PbI_3$

$E = 2.23\text{eV}$ $E = 3.00\text{eV}$

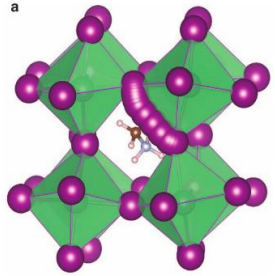


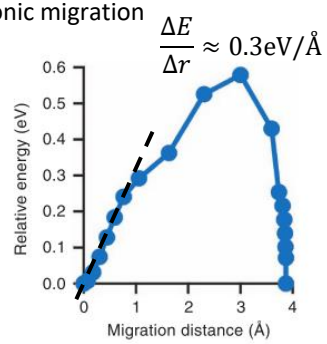


Distribution of forces



Theoretical study of the energy barrier for ionic migration





Eames et al, *Nat Comm*, 6, 7497 (2015)

Conclusions

- We calculated **excited state forces** in terms of **GW/BSE + DFPT** calculations
- Atomic forces in MAPI's cations are higher than forces in the cage
- Optical absorption may cause methylammonium vibration!
- Excited state forces are strong enough to cause ionic migration

Acknowledgements

NSF NERSC AFOSR AIR FORCE OFFICE OF SCIENTIFIC RESEARCH