DFT-Calculated Properties of Graphene Shield Enhanced Photocathodes

Jefferson Lab – P3 Workshop

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APPLIED CATHODE ENHANCEMENT AND ROBUSTNESS TECHNOLOGIES

My Collaborators

K.L. Jensen (NRL) quantum efficiency modeling

S.G. Lambrakos (NRL) organization collaboration

M.J. Mehl (USNA) DFT guru

A. Shabaev (GMU) solid-state genius

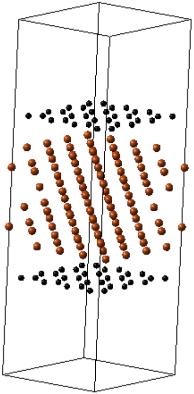
N.A. Moody (LANL) experimental realization!

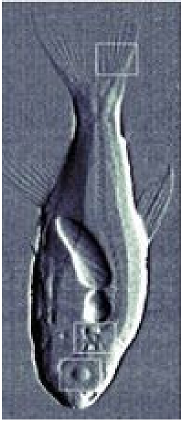
Outline

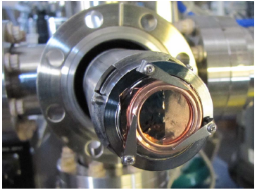
Motivation

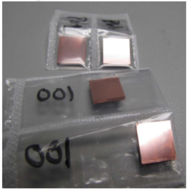
Key idea: Graphene is a transparent and tough gas barrier that is also inert on many surfaces; photoemission is therefore preserved while increasing cathode longevity! (credit goes to N.A. Moody)

Motivation

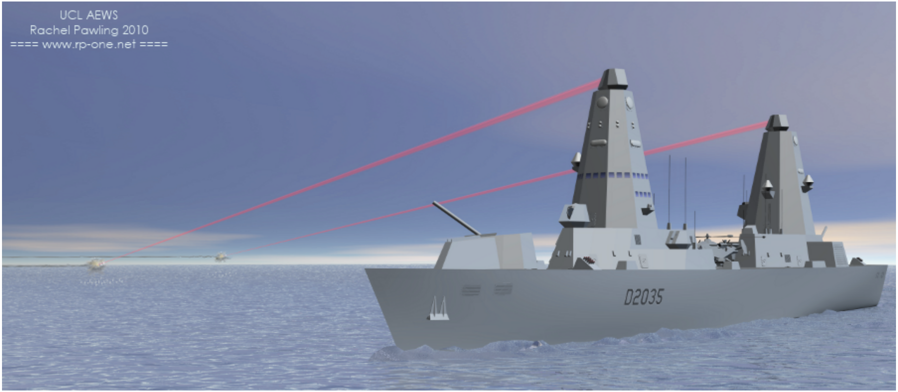




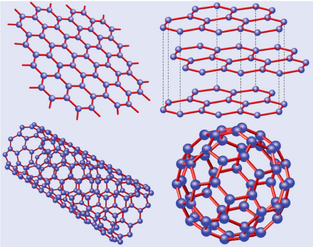


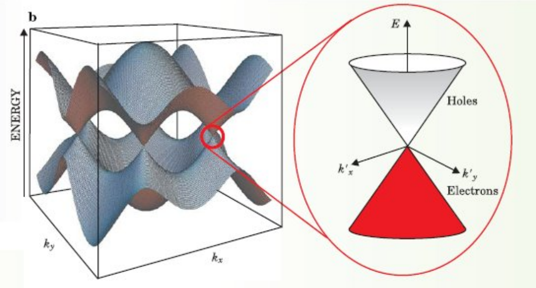


- science of **cathodes**
  - DFT predictions
- **Free electron lasers**
- Navy wants lasers
- DOE project: MaRIE
- medical applications

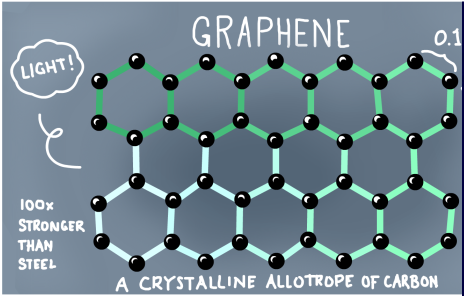

UCL AEWS
Rachel Pawling 2010
==== www.rp-one.net ====
D2035

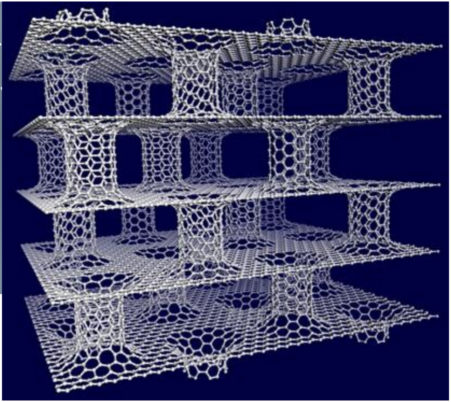
Graphene

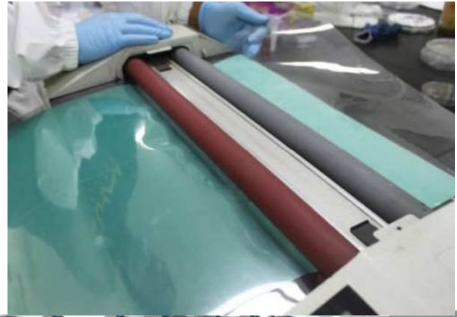




- E vs. $\vec{\mathbf{k}}$ similar to ~~photons~~ neutrinos!
- but with $c \simeq 1 \times 10^6\,\mathrm{m\,s^{-1}}$
- best conductor at room temperature







- **Huge sheets of it!**
- Transparent conductor; protector of cathodes!

2 math slides next; mostly 40 year old ideas, but I think relevant to problem.

DFT and related methods

DFT attempts to solve **[Kohn&Sham1965]**

$$\left(-\frac{1}{2}\Delta + v_{\mathrm{ext}}(\vec{\mathbf{r}}) + \int \mathrm{d}\vec{\mathbf{r}}' \frac{n(\vec{\mathbf{r}}')}{|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|} + v_{xc}[n]\right) \varphi_i(\vec{\mathbf{r}}) = \epsilon_i \varphi_i(\vec{\mathbf{r}})$$

- approximate v_{xc}, e.g. "local-density" (LDA)
- self-interaction but it's removable **[Perdew1981]**
- *in*exact correlation, but in LDA the errors tend to cancel with those of exchange
- Janak's theorem [**1978**]:

$$\boxed{\frac{\partial E^{KS}}{\partial n_i} = \epsilon_i}$$

Hartree-Fock

Hartree-Fock [**1920s**]

$$\left(-\frac{1}{2}\Delta + v_{\text{ext}}(\vec{\mathbf{r}})\right)\varphi_i(\vec{\mathbf{r}}) + \sum_j \int \mathrm{d}\vec{\mathbf{r}}' \frac{|\varphi_j(\vec{\mathbf{r}}')|^2}{|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|}\varphi_i(\vec{\mathbf{r}})$$

$$- \sum_j \delta_{\sigma_i,\sigma_j} \int \mathrm{d}\vec{\mathbf{r}}' \frac{\varphi_i(\vec{\mathbf{r}}')\varphi_j^*(\vec{\mathbf{r}}')}{|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|}\varphi_j(\vec{\mathbf{r}}) = \epsilon_i \varphi_i(\vec{\mathbf{r}})$$

- *no* self-interaction, *exact exchange*, order N^4 (DFT is N^3); *Is it any better than DFT?*
- Koopman's theorem [**1934**]:

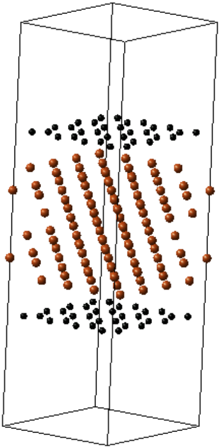
$$\boxed{E^{HF}(N) - E^{HF}(N-1) = \epsilon_{i,\ \text{occupied}}}$$

DFT and HF are both useful

- DFT is the most successful *theory* of all time
- $> 30,000$ papers per year
- it is not the end of the story however;
- photoionization is a nice problem that touches directly on what exactly you are asking for when you compare calculated energy eigenvalues to experimental excited state spectra

Results

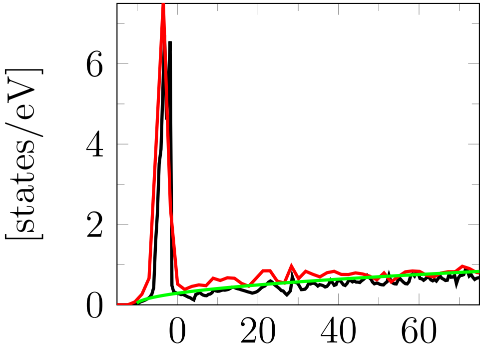
DFT Result: relaxation of Gr//Cu (111)



- VASP code
- mostly LDA
- relaxation of
  1. electronic w.f.'s
  2. electrostatic n
  3. electrostatic v
  4. atomic forces, coords.
- output:
  1. e^- DOS, spectra
  2. potential, work fcn

DFT Result: DOS of bulk Cu

Cu DOS: **LDA** vs. **HF**



- Used in Spicer model [K.L. Jensen]
    - really like free e^-?
- LDA (black), HF (red)
- free electron (green)

DFT Result: Cu Work Fcn

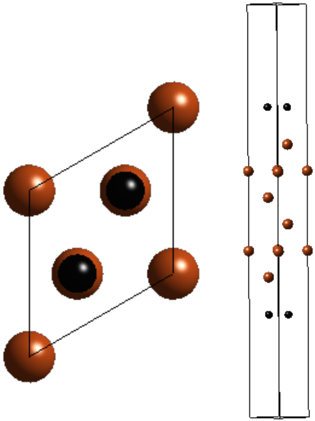
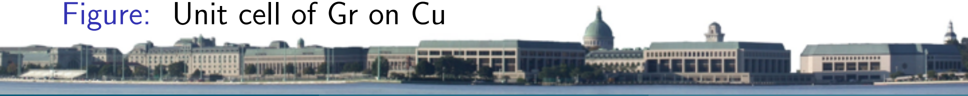


Figure: Unit cell of Gr on Cu

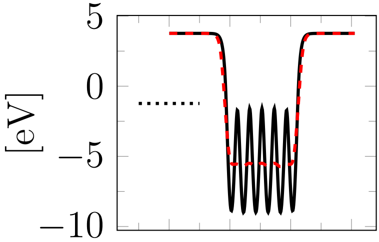
The following show

1. potential profiles $V(z)$
   - along z
   - thru Cu bulk,
   - thru Gr on Cu,
2. **average** the profiles
3. get fermi level ϵ_f

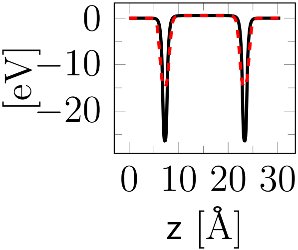
$$\phi = V^{\text{vac}} - \epsilon_f$$



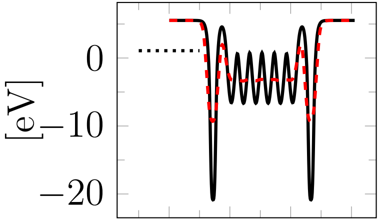
Cu 111: **LDA**



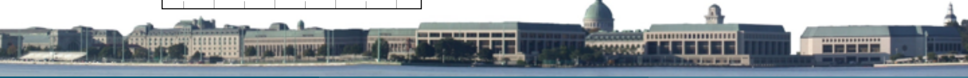
Graphene impurity



Gr on Cu 111



- $\phi = 5.00\,\text{eV}$, bulk Cu
- $\phi = 4.25\,\text{eV}$, Gr//Cu
- good trans. thru Gr

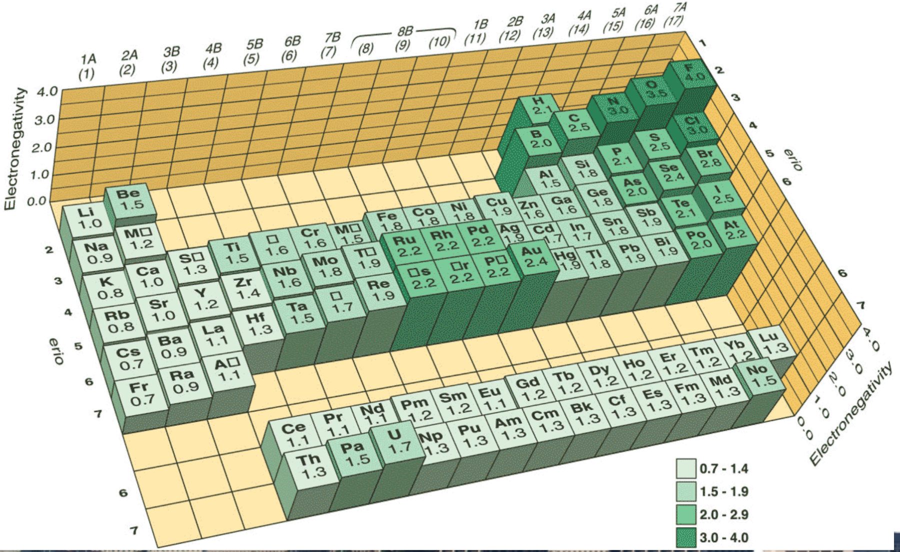


DFT Result: Gr on Cs_3Sb

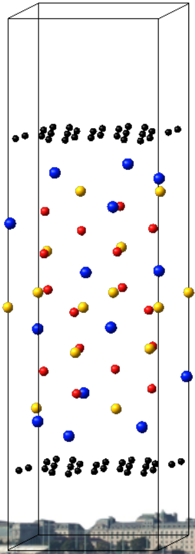
- $\phi_{\mathrm{cleanCs3Sb}} = 1.5\,\mathrm{eV} \rightarrow$
  - flat Gr 3.15 eV
  - buckled 3.55 eV
  - defects$\rightarrow$ 5.00 eV (?)
- Recall Gr on Cu gave 4.25 eV

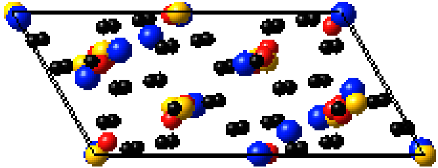
- Gr protects as gas barrier, but
- Gr increases ϕ on this system
- QUESTION: WHY?

ANS: electronegativity



DFT Result: Gr on K_2CsSb



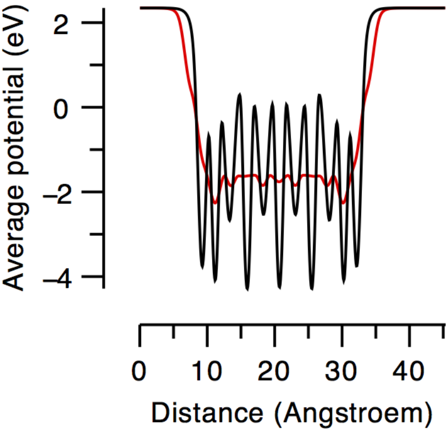


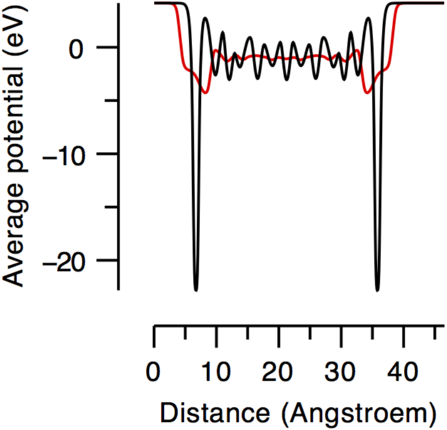
- Cs rich surface
- C, Cs, **K**, **Sb**
- $[111]$ direction (left)
- (111) planes (above)

- VASP ran for weeks

DFT Result: Gr on K_2CsSb

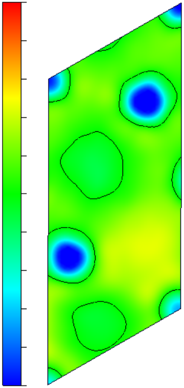
avg. potentials: $\phi = 1.75\,\text{eV}$ $\phi_{Gr} = 3.70\,\text{eV}$



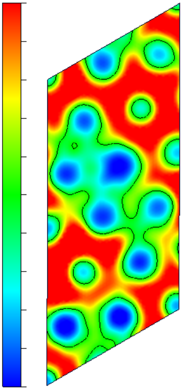


DFT Result: Gr on K_2CsSb

Why does Gr increase work fcn on Cs surface? **CHARGE**



Cs LOSS,



Gr GAIN

Direction of dipole

- Cs is most electropositive element
- so e^- transfer to Gr
- ϕ increases w/ these inward pointing dipoles

Conclusion

- Graphene can enhance and protect cathodes in theory *as well as in experiment*
- acts as a resonant well, assisting photoemission without much reflection

Some results not detailed here:

- Improved quantum efficiency for graphene on Cu 110
- Photoemission confirmed thru graphene on Cs_3Sb

Thank you!