Please limit to 10 min (presentation 7-8 minutes + questions 2 min)

Repeat the question on the first slide

Exercise 2.1 (Molecular Orbitals)

Please describe (preferably as a PPT presentation):

- The orbitals of a cyclic aromatic compound with N atoms are described by the Coulson formula:

$$E_q = \alpha + 2\beta \cos\left(\frac{2\pi q}{N}\right) \qquad q = 1,2,\ldots N$$

$$\psi_q = \sum_{n=1}^{N} a_n^q \psi_{2p_z}(n) \qquad a_n^q = \sqrt{\frac{1}{N}}\, e^{\left(\frac{2i\pi qn}{N}\right)}$$

a) Calculate the energies of the π molecular orbitals of benzene and represent them in an energy level diagram.

b) Applying the Pauli exclusion principle, calculate the energy lowering of the system (as compared to the isolated carbon atoms) induced by the bonding of the π electrons.

c) Calculate the wavefunctions with highest and lowest energy and sketch all the Hückel molecular orbitals.

Hint: the remaining wavefunctions are given by

$$\psi_5 = \frac{1}{\sqrt{12}}(2\psi_{p_z}(1) + \psi_{p_z}(2) - \psi_{p_z}(3) - 2\psi_{p_z}(4) - \psi_{p_z}(5) + \psi_{p_z}(6))$$

$$\psi_1 = \frac{1}{2}(\psi_{p_z}(2) + \psi_{p_z}(3) - \psi_{p_z}(5) - \psi_{p_z}(6))$$

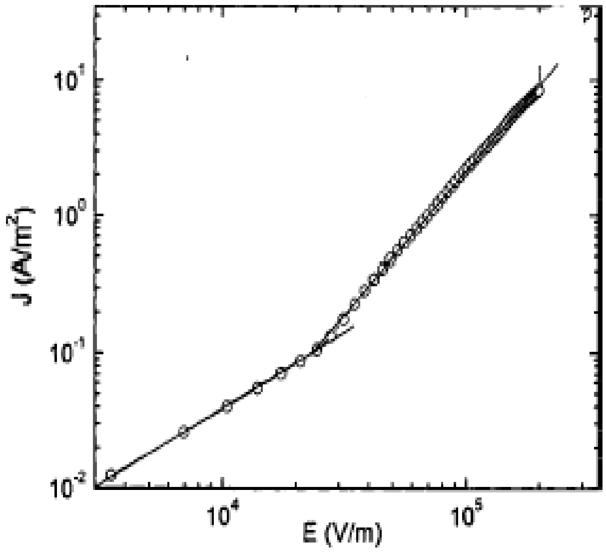
$$\psi_2 = \frac{1}{\sqrt{12}}(2\psi_{p_z}(1) - \psi_{p_z}(2) - \psi_{p_z}(3) + 2\psi_{p_z}(4) - \psi_{p_z}(5) - \psi_{p_z}(6))$$

$$\psi_4 = \frac{1}{2}(\psi_{p_z}(2) - \psi_{p_z}(3) + \psi_{p_z}(5) - \psi_{p_z}(6))$$

d) α and β, what do they stand for?

Exercise 2.2 (Mobility)

Please describe (preferably as a PPT presentation):



a) Estimate the charge carrier mobility in a conjugated organic single crystal from the current-voltage plot on the right. The data was obtained by sandwiching the 20 μm thick crystal between two gold electrodes. First determine which region of the current-voltage characteristics is governed by ohmic behavior and which is governed by space charge limited current. Explain why.

b) You expect to have measured the hole or electron mobility?

(Take ε=3 as the dielectric constant of the molecular solid)

c) How will the curve change in the presence of traps?

d) Suggest another experiment to test if you are really in the SCLC regime.

Exercise 2.3. (Efficient charge extraction in organic and perovskite solar cells)

Please describe (preferably as a PPT presentation):

The concept of cascading energy levels represents a sophisticated strategy employed in solar cell design to significantly enhance power conversion efficiency by optimizing charge transport pathways and minimizing energy losses. We have seen this for organic solar cells (2.2A No 22 & 32) and perovskites (2.3A no50).

a) Compare and contrast the architectural designs of regular and the so-called "inverted organic solar cells", detailing the typical layer stacking order and the role of the transparent electrode in each. Make a schematic drawing of the energy diagrams.

b) Draw energy diagrams for the n-i-p and p-i-n architectures in perovskite solar cells, identifying the key layers and their typical material compositions for both ETL and HTL.

c) What are good electrode materials? Why?

d) Why are frequently additional interfacial layers implemented?

e) What are the advantages of the inverted and p-i-n architecture?

Exercise 2.4. (Mixed halide solar cells)

Please describe (preferably as a PPT presentation):

Composition engineering plays a central role in the development of perovskite solar cells, as variations in the A-, B-, and X-site constituents allow optimization of both photovoltaic performance and crystal stability, the latter commonly evaluated using the Goldschmidt tolerance factor.

a) Explain the concept of "tolerance factor"

b) Calculate the tolerance factors for $MAPbI_3$, $NaPb I_3$, and $EDAPbB_3$ and explain with these examples how that is related to structural stability.

c) What happens when a cation with an unusually large ionic radius (typically greater than approximately 2.6 Å) is introduced as an A-site component in the perovskite structure (key word Ruddlesden-Popper perovskite). What does that mean for the tolerance factor?

d) Where do 2D perovskites find applications in Perovskite solar cells?

Literature:

Kieslich et al. Chem. Sci.,2015,6, 3430; https://doi.org/10.1039/c5sc00961h

Ramos-Terrón et al., Chem. Mater. 2020, 32, 9, 4024–4037; https://doi.org/10.1021/acs.chemmater.0c00613

Exercise 2.5. (Bandgap engineering in perovskites)

Please describe (preferably as a PPT presentation):

Lead halide perovskite semiconductors offer several possibilities to tune the bandgap and to alter the band gap energy.

a) Explain by which way the band gap in these semiconductors can be tuned and give the achievable range of energies.

b) Why is it interesting to vary the bandgap in solar cells?

Unusual about many metal-halide perovskites is that the band gap is formed between antibonding states rather than between a bonding and an antibonding state, as in many conventional semiconductors.

c) Draw a simple, qualitative 2-level Molecular Orbital (MO) energy diagram showing the interaction between the Pb 6s orbital (on the left) and the Halogen p orbital (on the right) for a generic lead halogen perovskite. Which atomic orbitals hybridize to form the Valence Band Maximum (VBM)? Which atomic orbitals primarily make up the Conduction Band Minimum (CBM)?

d) Why does substituting the halogen have a massive impact on the VBM energy level but very little impact on the CBM energy level?

e) As you move down the halogen column of the periodic table from Chlorine to Bromine to Iodine: state what happens to the atomic size and the electronegativity of the halogen. Based on these periodic properties, explain what happens to the energy level of the outermost - orbitals of the halide anions.

f) What is now the consequence for the bandgap?

Literature:

Noh et al., Nano Lett. 2013, 13, 1764−1769; https://doi.org/10.1021/nl400349b

Diagram from lecture 2.3. slide 20

Tao et al., Nature Communications 2019, 10:2560;
https://doi.org/10.1038/s41467-019-10468-7

Exercise 2.6. (Defect passivation in perovskites)

Please describe (preferably as a PPT presentation):

Despite their impressive performance metrics, PSCs face a critical hurdle to widespread commercialization: their inherent instability. Devices often exhibit a rapid efficiency drop shortly after fabrication, a phenomenon primarily attributed to the presence of a high density of defects within the perovskite film. Defect passivation has emerged as a widely studied method to enhance both the stability and efficiency of PSCs by mitigating defects.

a) What is the primary purpose of employing passivation strategies in the fabrication of perovskite solar cells?

b) In the context of perovskite defects, what type of defect is an undercoordinated lead ion ($Pb2^+$)?

c) Which type of chemical interaction is commonly used to passivate electron-deficient defects like lead vacancies in perovskites?

d) How do 2D perovskites typically passivate a 3D perovskite film in a 2D/3D heterostructure?

e) Grain boundary passivation is a critical strategy. Why are grain boundaries in polycrystalline perovskite films particularly problematic?

f) What is a common experimental technique used to demonstrate the successful passivation of defects by measuring the reduction in non-radiative recombination?

Literature:

Many comprehensive sources around, e.g.:

Huang et al., Mater. Chem. Front., 2024, 8, 3528–3557

https://doi.org/10.1039/d4qm00560k