ELASTICITY

When an elastic material is stretched, it returns to its original position. But when it's over stretched beyond its limit point, it loses its elasticity and becomes plastic, and later cuts or breaks.

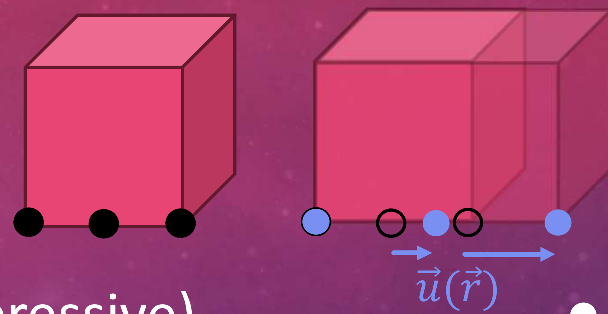
-Richmond Akhigbe

THIS LECTURE

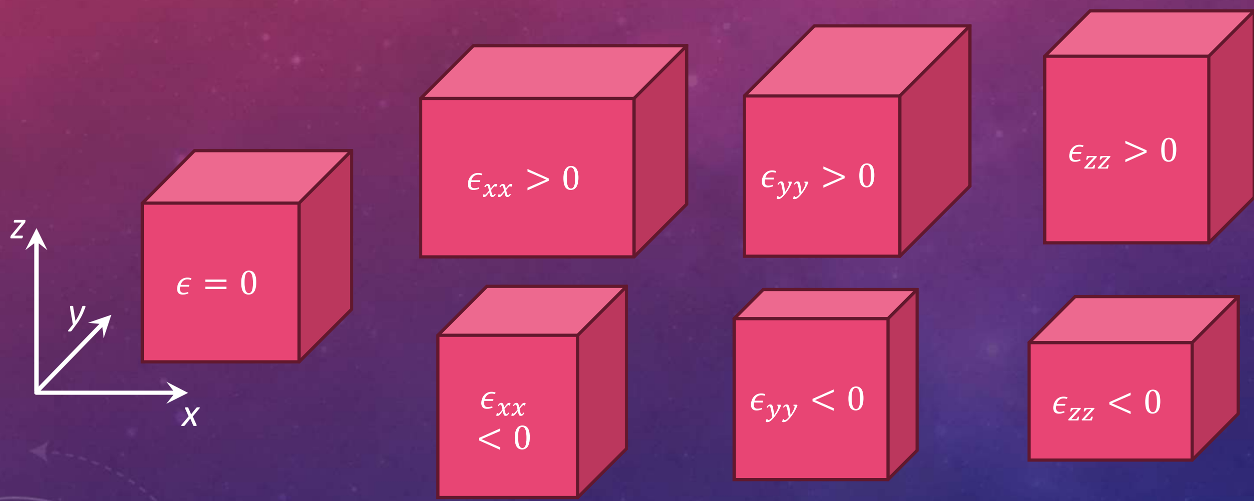
- Introduction to elasticity: strain and stress
- Elastic energy for bulk materials (with applications)
- Chemical stress and strain
- *Ab initio* theory of stress and elastic constants
- Examples

CONCEPT OF STRAIN

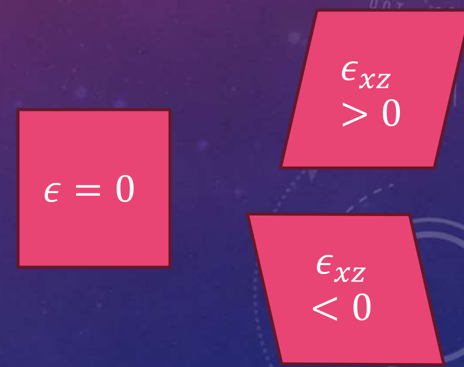
- Deformation of a material



- Linear strain (+=tensile, -=compressive)



- xz shear strain (also xy and yz)



- Definition: Given displacements $\vec{u}(\vec{r})$, $\epsilon_{ij} \equiv \frac{1}{2}\left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i}\right)$ with $i, j = x, y, z$

CONCEPT OF STRESS

- Measure of restoring force

- Stress $\overleftrightarrow{\sigma}$ is analogous to pressure
  - Acts across a surface
  - Direction of force determined by surface normal
  - Defined as force per unit area
  - Sign is different (+ stress wants to contract)
  - Is a tensor instead of a scalar (*P* corresponds to diagonal tensor)

$\vec{F}/A \equiv -\overleftrightarrow{\sigma} \cdot \hat{n}$

- Obeys Hooke's Law:
  $\sigma_{ij} = \sum_{kl} C_{ij;kl} \epsilon_{kl}$ (physics)
  $\sigma_\alpha = \sum_\beta C_{\alpha\beta} \epsilon_\beta$ with $\alpha, \beta = xx, yy, zz, xy, xz, yz \equiv 1 \ldots 6$ (engineering)

- For cubic symmetry: $\boldsymbol{C_{11}} = C_{22} = C_{33}, \boldsymbol{C_{12}} = C_{13} = C_{23}, \boldsymbol{C_{44}} = C_{55} = C_{66}$
  (rest are 0)

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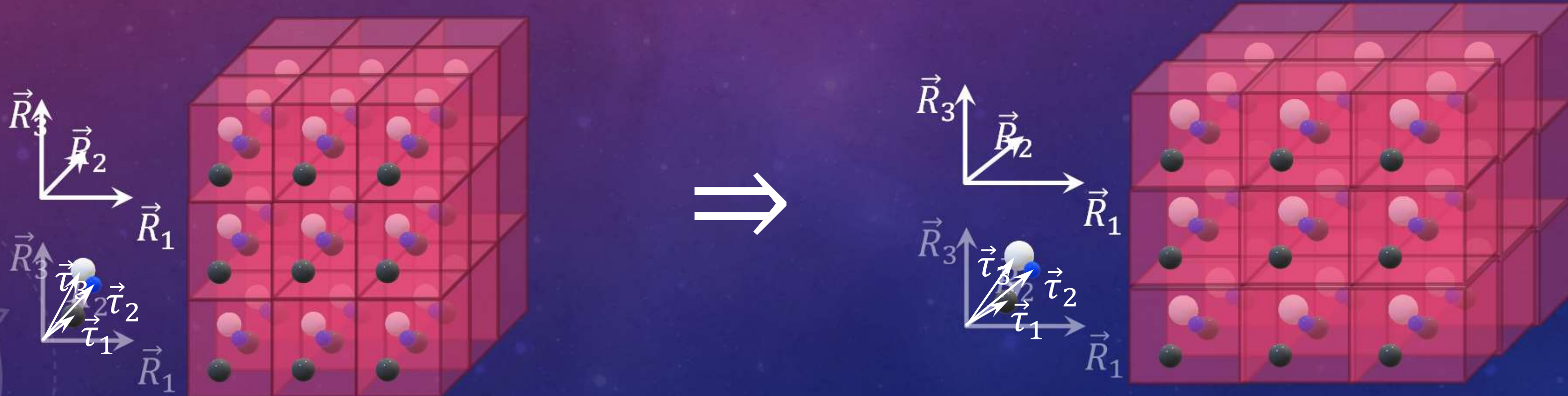
STRESS, STRAIN AND *ENERGY*

$\vec{F}/A \equiv -\overleftrightarrow{\sigma}\cdot\hat{n}$

- Define energy per unit volume $u = \frac{E}{V}$
- Work from $\vec{F}/A \equiv -\overleftrightarrow{\sigma}\cdot\hat{n}$ implies $\sigma_{ij} = \frac{\partial u}{\partial \epsilon_{ij}}$
- Application:

  Can find ideal strain/lattice vectors from gradient descent:

  $$\circlearrowright\ \epsilon_{ij} \leftarrow \epsilon_{ij} - \delta \cdot \frac{\partial u}{\partial \epsilon_{ij}} = \epsilon_{ij} - \delta \cdot \sigma_{ij}$$



STRESS, STRAIN AND *ENERGY*

Total strain energy

Equating Hooke's law $\sigma_{ij} = \sum_{kl} C_{ij;kl}\epsilon_{kl}$ with $\sigma_{ij} = \frac{\partial u}{\partial \epsilon_{ij}}$ gives …

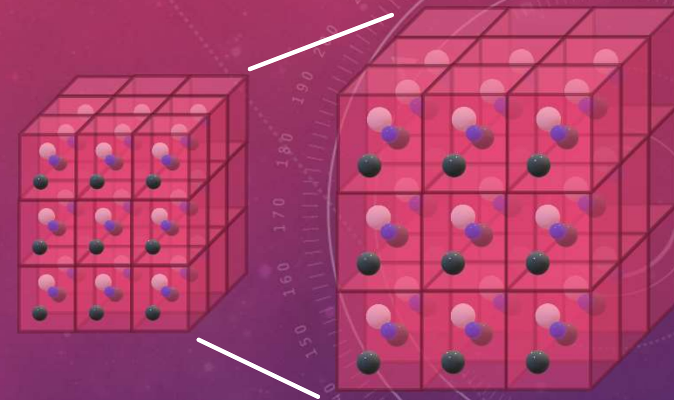
$$\frac{\partial u}{\partial \epsilon_{ij}} = \sum_{kl} C_{ij;kl}\epsilon_{kl} \Rightarrow$$

$$\Delta u_{\text{strain}} = \frac{1}{2}\sum_{ij;kl} \epsilon_{ij}\, C_{ij;kl}\epsilon_{kl}$$

$$\Delta u_{\text{strain}} = \frac{1}{2}\sum_{\alpha\beta} \epsilon_{\alpha}\, C_{\alpha\beta}\, \epsilon_{\beta} \quad \text{(Engineering)}$$

$$(\alpha, \beta = xx, yy, zz, xy, xz, yz \equiv 1 \ldots 6)$$

STRESS, STRAIN AND *ENERGY*



- Strain Energy (1): Cubic system, Isotropic strain

$$\overleftrightarrow{\epsilon} = \begin{pmatrix} \epsilon_1 & \epsilon_4 & \epsilon_5 \\ \epsilon_4 & \epsilon_2 & \epsilon_6 \\ \epsilon_5 & \epsilon_6 & \epsilon_3 \end{pmatrix} = \begin{pmatrix} \eta & & \\ & \eta & \\ & & \eta \end{pmatrix}$$

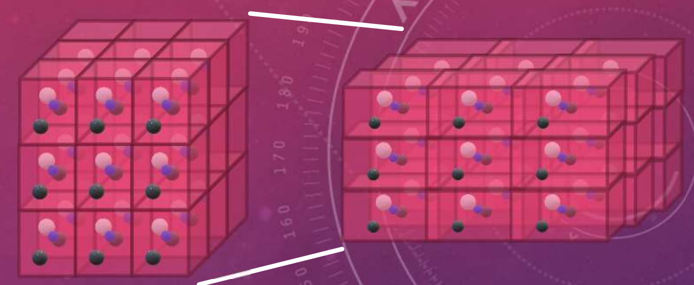
$$\epsilon_1 = \epsilon_2 = \epsilon_3 = \eta; \epsilon_4 = \epsilon_5 = \epsilon_6 = 0 \; (xx, yy, zz, xy, xz, yz)$$

- $\Delta u_{\text{strain}} = \frac{1}{2} \sum_{\alpha\beta} \epsilon_\alpha \, C_{\alpha\beta} \, \epsilon_\beta$

$$= \frac{1}{2}\{C_{11}(\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2) + C_{44}(\epsilon_4^2 + \epsilon_5^2 + \epsilon_6^2) + C_{12}(2\epsilon_1\epsilon_2 + 2\epsilon_1\epsilon_3 + 2\epsilon_2\epsilon_3)\}$$

$$= \frac{3}{2}\,(C_{11} + 2C_{12})\,\eta^2$$

STRESS, STRAIN AND *ENERGY*



- Strain Energy (2): Cubic system, Isovolumetric strain

$$\overleftrightarrow{\epsilon} = \begin{pmatrix} \epsilon_1 & \epsilon_4 & \epsilon_5 \\ \epsilon_4 & \epsilon_2 & \epsilon_6 \\ \epsilon_5 & \epsilon_6 & \epsilon_3 \end{pmatrix} = \begin{pmatrix} 2\eta & & \\ & -\eta & \\ & & -\eta \end{pmatrix}$$

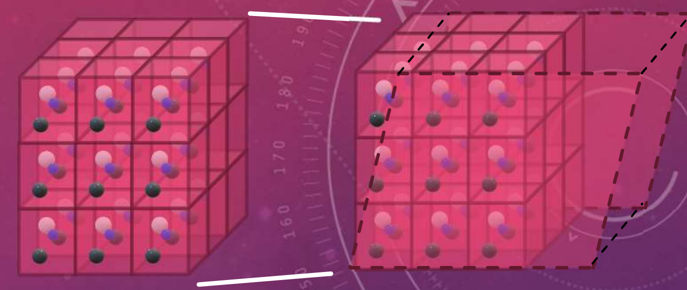
$$\epsilon_1 = 2\eta, \epsilon_2 = -\eta,\ \epsilon_3 = -\eta;\ \ \epsilon_4 = \epsilon_5 = \epsilon_6 = 0\ (xx, yy, zz, xy, xz, yz)$$

- $\Delta u_{\text{strain}} = \frac{1}{2} \sum_{\alpha\beta} \epsilon_\alpha\, C_{\alpha\beta}\, \epsilon_\beta$

$$= \frac{1}{2}\left\{C_{11}\left(\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2\right) + C_{44}\left(\epsilon_4^2 + \epsilon_5^2 + \epsilon_6^2\right) + C_{12}\left(2\epsilon_1\epsilon_2 + 2\epsilon_1\epsilon_3 + 2\epsilon_2\epsilon_3\right)\right\}$$

$$= 3\ (C_{11} - C_{12})\ \eta^2$$

STRESS, STRAIN <u>AND</u> *ENERGY*



- Strain Energy (3): Cubic system, Pure Shear

$$\overleftrightarrow{\epsilon} = \begin{pmatrix} \epsilon_1 & \epsilon_4 & \epsilon_5 \\ \epsilon_4 & \epsilon_2 & \epsilon_6 \\ \epsilon_5 & \epsilon_6 & \epsilon_3 \end{pmatrix} = \begin{pmatrix} & & \eta \\ & & \\ \eta & & \end{pmatrix}$$

$$\epsilon_1 = \epsilon_2 = \epsilon_3 = 0; \epsilon_4 = \epsilon_6 = 0, \epsilon_5 = \eta \ (xx, yy, zz, xy, xz, yz)$$

- $\Delta u_{\text{strain}} = \frac{1}{2} \sum_{\alpha\beta} \epsilon_\alpha \, C_{\alpha\beta} \, \epsilon_\beta$

$$= \frac{1}{2} \{ C_{11}(\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2) + C_{44}(\epsilon_4^2 + \epsilon_5^2 + \epsilon_6^2) + C_{12}(2\epsilon_1\epsilon_2 + 2\epsilon_1\epsilon_3 + 2\epsilon_2\epsilon_3) \}$$

$$= \frac{1}{2} \, C_{44} \, \eta^2$$

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RELATION OF STRESS AND STRAIN TO ENERGY

Chemical stress and strain

- For small strain ϵ_{ij} and volume concentration of defects c, expand …

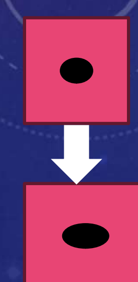
$$u(\epsilon, c) = u(\epsilon, c=0) + \frac{\partial u(\epsilon,c=0)}{\partial c} c + \sum_{ij} \frac{\partial u(\epsilon,c=0)}{\partial \epsilon_{ij}} \epsilon_{ij}$$

$$+ \sum_{ij} \frac{\partial^2 u(\epsilon,c=0)}{\partial c \partial \epsilon_{ij}} c\epsilon_{ij} + \frac{1}{2}\sum_{ij;kl} \epsilon_{ij} \frac{\partial^2 u(\epsilon,c=0)}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \epsilon_{kl} + \cdots$$

$$= u_0 + E^{(d)} c + c \sum_{ij} \sigma_{ij}^{(d)} \epsilon_{ij} + \frac{1}{2}\sum_{ij;kl} \epsilon_{ij} C_{ij;kl} \epsilon_{kl}$$

($E^{(d)}$=energy/defect)

- $\sigma_{ij} = \frac{\partial u}{\partial \epsilon_{ij}} = c\, \sigma_{ij}^{(d)} + \sum_{kl} C_{ij;kl} \epsilon_{kl}$: defects generate stress, $\sigma_{ij}^{(d)}$ = chemical stress tensor



- The minimum energy of the crystal occurs when $\sigma_{ij} = 0$

$\Rightarrow \epsilon_{ij} = c \left(-\sum_{kl} [C^{-1}]_{ij;kl}\, \sigma_{kl}^{(d)} \right) \equiv c\, \epsilon_{ij}^{(d)}$, $\epsilon_{ij}^{(d)}$ = chemical strain tensor

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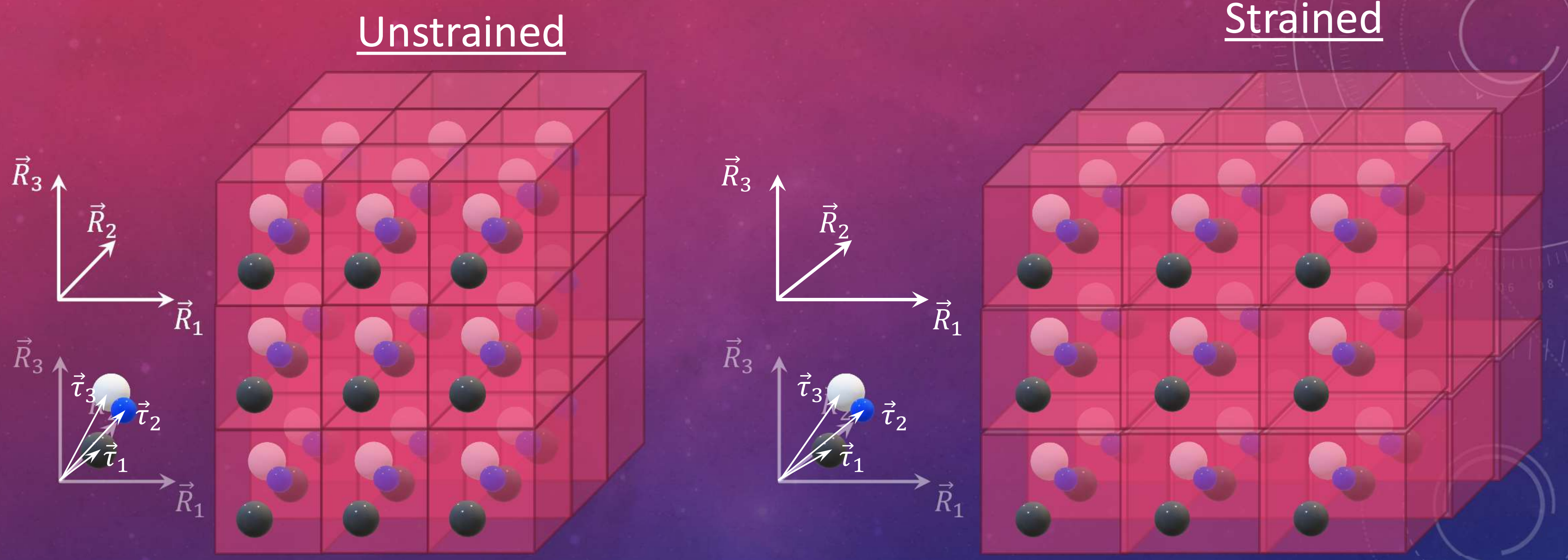
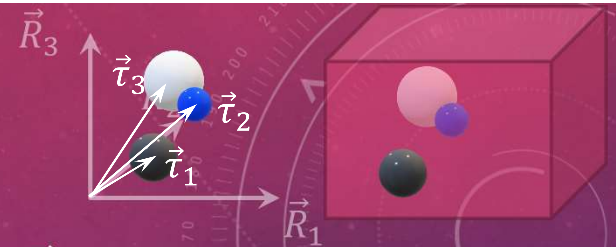
AB INITIO THEORY OF STRESS



- System described by $\vec{R}_\alpha(\epsilon_{ij}) = (I + \overleftrightarrow{\epsilon})\vec{R}_\alpha^{(0)}$ and $\vec{\tau}_I, \psi_{n\vec{k}}$

HELLMANN-FEYNMAN THEOREM FOR STRESS



- Definition of stress:

$$\sigma_{ij} \equiv \frac{du}{d\epsilon_{ij}} = \frac{1}{V_{\text{cell}}}\frac{d}{d\epsilon_{ij}}E_0(\epsilon_{ij}), \text{ where } E_0(\epsilon_{ij}) = \min_{\psi_{n\vec{k}},\vec{\tau}_I} E_0(\vec{R}_\alpha(\epsilon_{ij}), \vec{\tau}_I, \psi_{n\vec{k}})$$

- Define $\psi_{n\vec{k}}^{(0)}(\epsilon_{ij}), \vec{\tau}_I^{(0)}(\epsilon_{ij}) \equiv \arg\min_{\psi_{n\vec{k}},\vec{\tau}_I} E_0(\vec{R}_\alpha(\epsilon_{ij}), \vec{\tau}_I, \psi_{n\vec{k}})$, so that

$$E_0(\epsilon_{ij}) \equiv E_0(\vec{R}_\alpha(\epsilon_{ij}), \vec{\tau}_I^{(0)}(\epsilon_{ij}), \psi_{n\vec{k}}^{(0)}(\epsilon_{ij}))$$

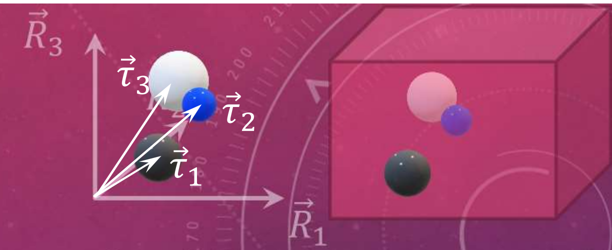
- Then, $\sigma_{ij} = \frac{1}{V_{\text{cell}}}\frac{d}{d\epsilon_{ij}}E_0(\vec{R}_\alpha(\epsilon_{ij}), \vec{\tau}_I^{(0)}(\epsilon_{ij}), \psi_{n\vec{k}}^{(0)}(\epsilon_{ij}))$

$$= \frac{1}{\mathrm{V}_{\text{cell}}}\left(\sum_\alpha \frac{\partial E_0}{\partial \vec{R}_\alpha}\frac{d\vec{R}_\alpha}{d\epsilon_{ij}} + \sum_I \cancel{\frac{\partial E_0}{\partial \vec{\tau}_I}}\frac{d\vec{\tau}_I^{(0)}}{d\epsilon_{ij}} + \sum_I \cancel{\frac{\partial E_0}{\partial \psi_{n\vec{k}}}}\frac{d\psi_{n\vec{k}}^{(0)}}{d\epsilon_{ij}}\right)$$

$$= \frac{1}{\mathrm{V}_{\text{cell}}}\sum_\alpha \frac{d\vec{R}_\alpha}{d\epsilon_{ij}}\frac{\partial}{\partial \vec{R}_\alpha}E_0(\vec{R}_\alpha(\epsilon_{ij}), \vec{\tau}_I^{(0)}(\epsilon_{ij}), \psi_{n\vec{k}}^{(0)}(\epsilon_{ij}))$$ (🤓!)

- Only need $\vec{\tau}_I^{(0)}(\epsilon_{ij}), \psi_{n\vec{k}}^{(0)}(\epsilon_{ij})$ from total energy calculation! (🤓!!!)

AB INITIO COMPUTATION OF ELASTIC MODULI



- For small distortions, $\sigma_{ij} = \sum_{jk} C_{ij;kl}\epsilon_{kl} \Rightarrow C_{ij;kl} = \frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}}$
- Extract linear coefficient with central difference for small $\Delta\epsilon$ …

For all kl: $\circlearrowright\ C_{ij;kl} = \frac{\sigma_{ij}(\overleftrightarrow{\epsilon}=+\delta_{kl}\cdot\Delta\epsilon) - \sigma_{ij}(\overleftrightarrow{\epsilon}=-\delta_{kl}\cdot\Delta\epsilon)}{2\cdot\Delta\epsilon}$

I.e.,

$C_{ij;kl}$ = [σ_{ij}() - σ_{ij}()] / $2\cdot\Delta\varepsilon$

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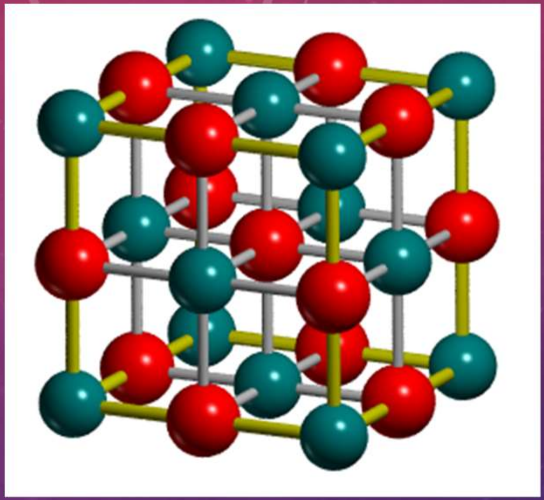
AB INITIO COMPUTATION OF ELASTIC MODULI

Rocksalt MgO



	a (Å)	E_0 (eV per MgO)	$B = \frac{C_{11}+2C_{12}}{3}$ (Mbar)
Expt	4.21	10.33	1.55-1.62
LDA	4.161 (-1.1%)	11.80 (+14%)	1.71 (+7.9%)
GGA	4.221 (+0.3%)	10.4 (+0.7%)	1.64 (+3.4%)

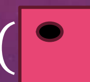
Daykov, Engeness, Arias, *PRL*
DOI: 10.1103/PhysRevLett.90.216402

AB INITIO CHEMICAL STRESS AND STRAIN

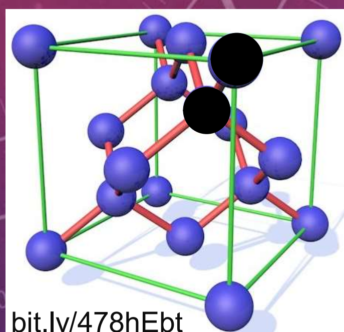
$$\sigma_{ij} = \frac{\partial u}{\partial \epsilon_{ij}} = c\,\sigma_{ij}^{(d)} + \sum_{kl} C_{ij;kl}\epsilon_{kl}$$

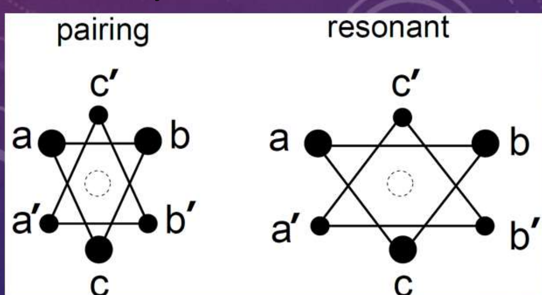
Add 1 defect to supercell, $\Delta\sigma_{ij} = \left(\frac{1}{V_{\text{cell}}}\right)\sigma_{ij}^{(d)}$:

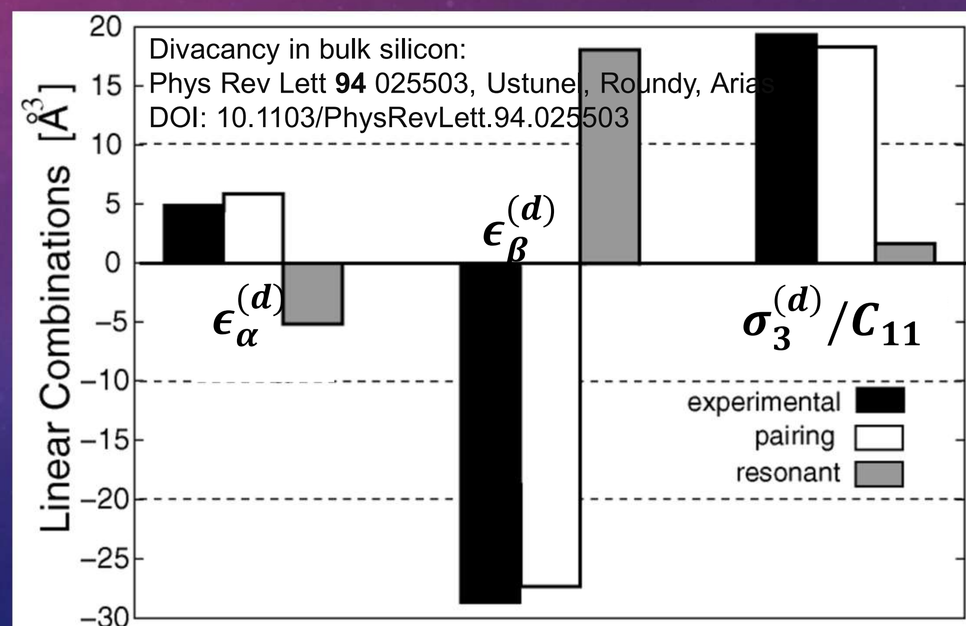
$$\Rightarrow \sigma_{ij}^{(d)} = V_{\text{cell}}\left(\sigma_{ij}(\text{w defect}) - \sigma_{ij}(\text{wo defect})\right) = V_{\text{cell}}\left(\sigma_{ij}(\ \ ) - \sigma_{ij}(\ \ )\right)$$

Divacancy defect in Si





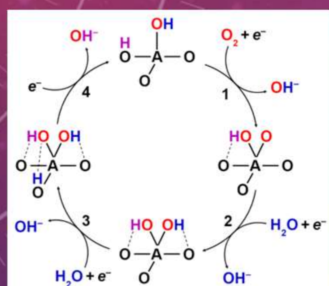


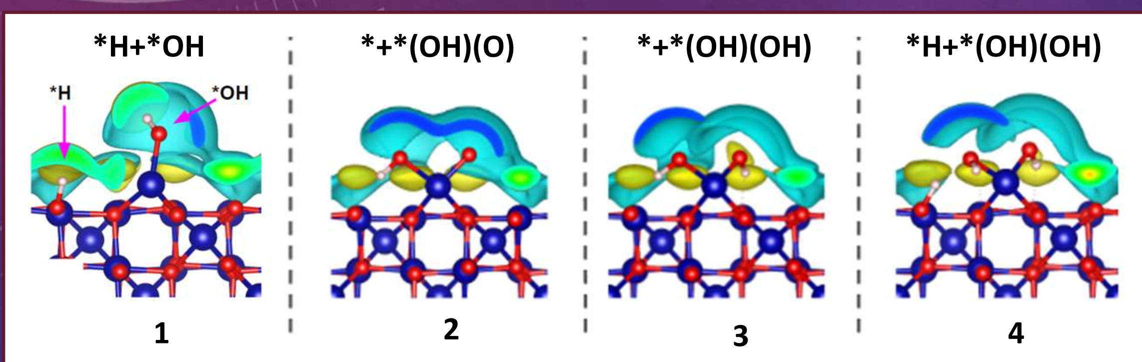
CHEMICAL SURFACE STRESS TENSOR

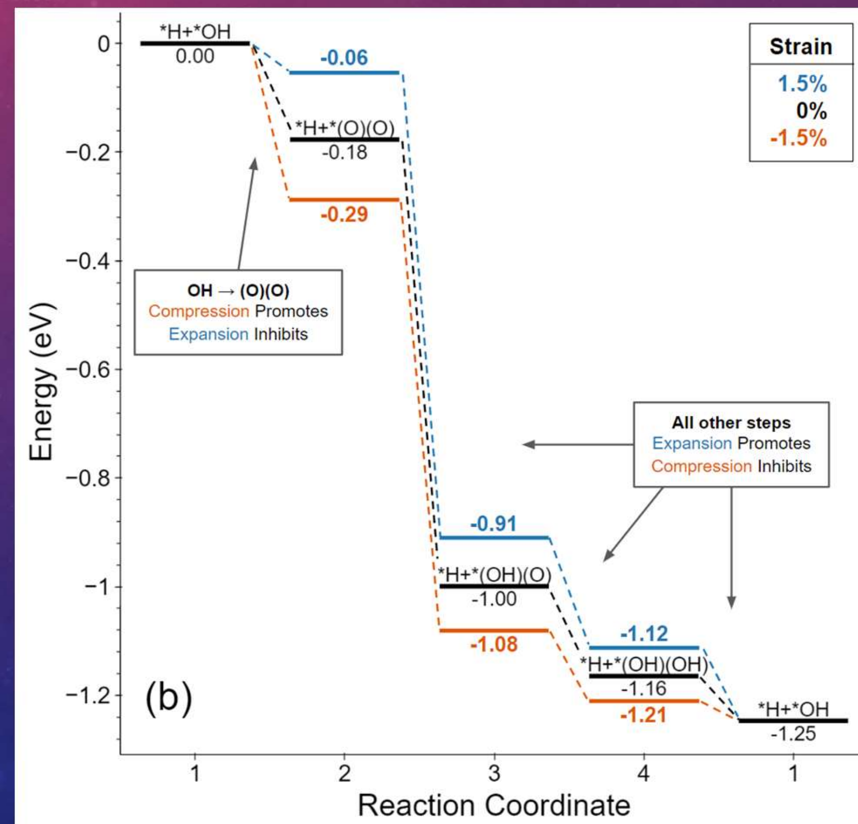
$$\frac{\Delta E_{\text{ads}}}{\Delta A} \equiv \gamma \sum_{ij} s_{ij}^{(d)} \epsilon_{\text{ij}}^{\text{surf}}$$, γ=adsorbate surface density

$$s_{ij}^{(d)} = V_{\text{cell}}\left[\sigma_{ij}(\text{w adsorbate}) - \sigma_{ij}(\text{wo adsorbate})\right]_{2\times2}$$

Alkaline ORR on Co_3O_4 spinel







Bundschu ... Arias, to be submitted

THANK YOU!

TAA2@CORNELL.EDU