2x2 Matrices cover much physics

(a) Find the eigenvalues of

$$\begin{pmatrix} \varepsilon_a & V_{ab} \\ V_{ab} & \varepsilon_b \end{pmatrix}, \quad \text{i.e. } (\varepsilon_a - \varepsilon)(\varepsilon_b - \varepsilon) - V_{ab}^2 = 0$$

solve for ε

$$\varepsilon = \frac{\varepsilon_a + \varepsilon_b}{2} \pm \frac{1}{2}\sqrt{(\varepsilon_a + \varepsilon_b)^2 - 4(\varepsilon_a \varepsilon_b - V_{ab}^2)} \quad (*)$$

$$= \frac{\varepsilon_a + \varepsilon_b}{2} \pm \frac{\varepsilon_a - \varepsilon_b}{2} \cdot \sqrt{1 + \frac{4V_{ab}^2}{(\varepsilon_a - \varepsilon_b)^2}}$$

exact so far.

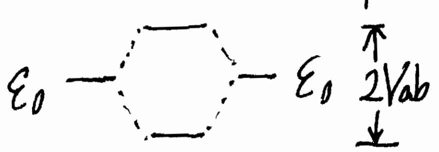
Two special cases

(b) $\varepsilon_a = \varepsilon_b = \varepsilon_0$

Start from (*), we have

$$\varepsilon = \begin{cases} \varepsilon_0 + V_{ab} \\ \varepsilon_0 - V_{ab} \end{cases}$$

i.e., Two degenerate states push each other apart

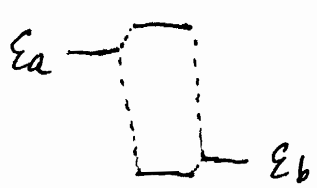


e.g. H_2

(c) $|\varepsilon_a - \varepsilon_b| \gg V_{ab}$

$$\varepsilon \approx \frac{\varepsilon_a + \varepsilon_b}{2} \pm \frac{\varepsilon_a - \varepsilon_b}{2}\left(1 + \frac{2V_{ab}^2}{(\varepsilon_a - \varepsilon_b)^2}\right)$$

$$\approx \begin{cases} \varepsilon_a + \dfrac{V_{ab}^2}{\varepsilon_a - \varepsilon_b} \\ \varepsilon_b - \dfrac{V_{ab}^2}{\varepsilon_a - \varepsilon_b} \end{cases}$$



e.g. HF

$$\varepsilon \approx \begin{cases} \varepsilon_a + \dfrac{V_{ab}^2}{\varepsilon_a - \varepsilon_b} \\ \varepsilon_b - \dfrac{V_{ab}^2}{\varepsilon_a - \varepsilon_b} \end{cases}$$

"A Pictorial Image in mind"...

- States repel each other in energy

  i.e., state of high energy (e.g. ε_a) is pushed up in energy by the state(s) of lower energy (energies)

  AND

  state of lower energy (e.g. ε_b) is pushed down in energy by the state(s) of high energy (energies)

- Case (c) is essentially the 2nd order non-degenerate ($\varepsilon_a \neq \varepsilon_b$) perturbation theory in QM
- Case (b) is essentially the degenerate ($\because \varepsilon_a = \varepsilon_b$) perturbation theory in QM

Applications

- Two atoms far apart ⇒ one is not affecting the other

energy of atomic orbital of relevance in atom A (e.g. 1s orbital in H)

$$\begin{pmatrix} \varepsilon_a & 0 \\ 0 & \varepsilon_b \end{pmatrix}$$

Far apart, atoms A & B are not influcencing each other

energy of atomic orbital of relevance in atom B

- Two atoms get closer ⇒ $\begin{cases} \text{one is affecting the other} \\ \text{formation of molecule} \end{cases}$

$$\begin{pmatrix} \varepsilon_a & V_{ab} \\ V_{ab} & \varepsilon_b \end{pmatrix}$$

describes how atoms A & B influence each other: "interaction energy"