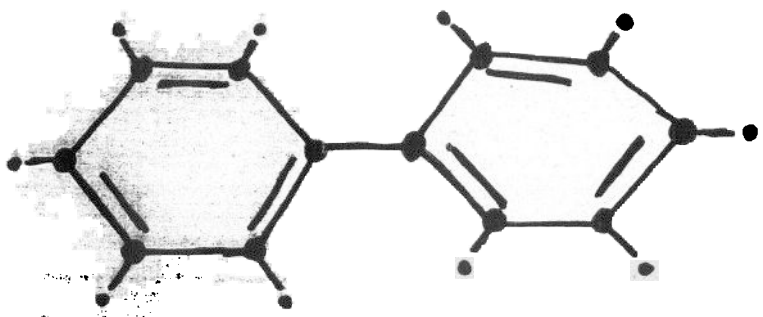
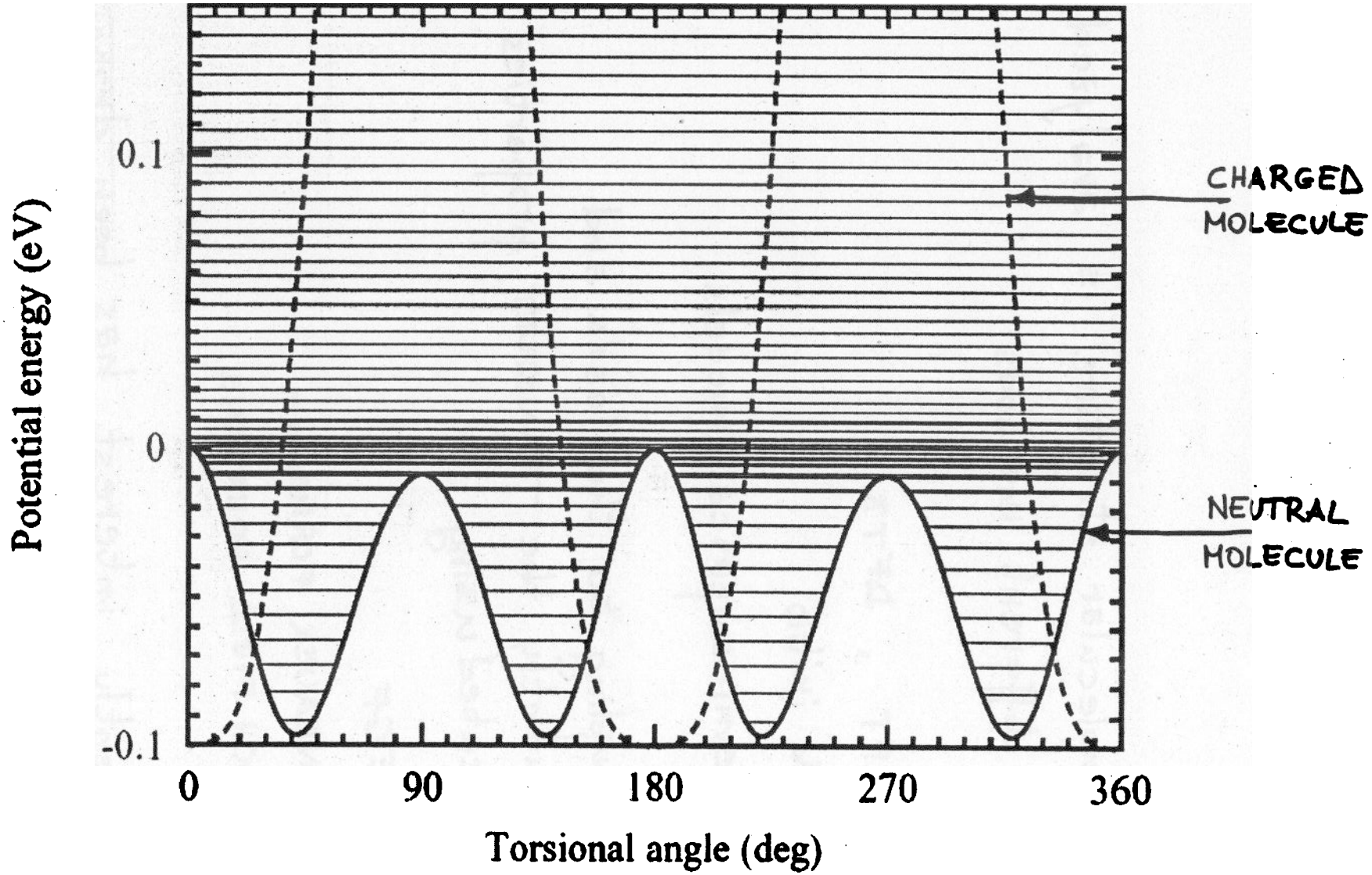
Biphenyl Molecule

preliminaries to transport




Potential energy (eV)
0.1
0
-0.1
0
90
180
270
360
Torsional angle (deg)
CHARGED MOLECULE
NEUTRAL MOLECULE

Methods

- The molecular structure is analyzed using different methods:

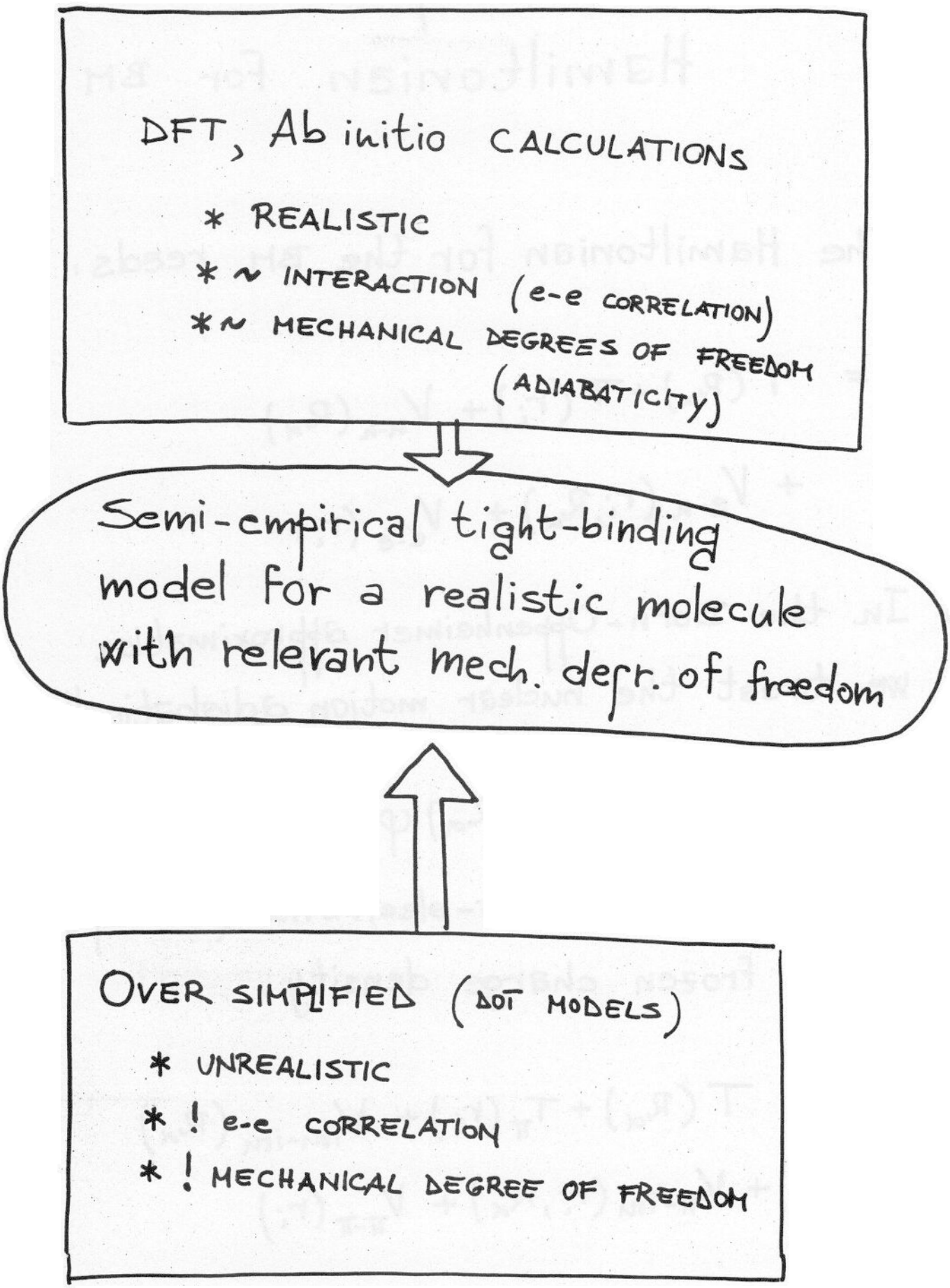
  * DFT , DFTB
  * Ab initio
  * Semi-empirical models

- The coupling to the leads and consequently the TRANSPORT properties are treated using:

  * NEGF
  * LANDAUER FORMALISM
  * BLOCH FIELD EQUATIONS

Only recently interest has been drawn on the effects of the MECHANICAL Degree of freedom on electrical transport.

Goals


DFT, Ab initio CALCULATIONS
* REALISTIC
* ~ INTERACTION (e-e CORRELATION)
* ~ MECHANICAL DEGREES OF FREEDOM (ADIABATICITY)
Semi-empirical tight-binding model for a realistic molecule with relevant mech. degr. of freedom
OVER SIMPLIFIED (DOT MODELS)
* UNREALISTIC
* ! e-e CORRELATION
* ! MECHANICAL DEGREE OF FREEDOM

Pariser-Parr-Pople Hamiltonian For BM

- The Hamiltonian for the BM reads:

$$H = T(R_\alpha) + T(r_i) + V_{n\text{-}n}(R_\alpha) + V_{e\text{-}n}(r_i, R_\alpha) + V_{e\text{-}e}(r_i)$$

- In the Born-Oppenheimer approximation we treat the nuclear motion adiabatically

$$\Psi(R_\alpha, r_i) = \chi(R_\alpha)\,\varphi(R_\alpha, r_i)$$

- We treat the CORE σ-electrons (C in sp_2) as a frozen charge density.

$$H = T(R_\alpha) + T_\pi(r_i) + V_{im\text{-}im}(R_\alpha) + V_{\pi\text{-}im}(r_i, R_\alpha) + V_{\pi\text{-}\pi}(r_i)$$

P-P-P Hamiltonian (II)

- The ion dynamics is described by the equation:

$$\left[T_\theta + V_{ion\text{-}ion}(\theta) + \varepsilon(\theta)\right]\chi(\theta) = E\,\chi(\theta)$$

where the contribution $\varepsilon(\theta)$ is the el. energy:

$$\left[T_\pi + V_{\pi\text{-}ion} + V_{\pi\text{-}\pi}\right]\varphi(\theta, r_i) = \varepsilon(\theta)\varphi(\theta, r_i)$$

- The ion-ion contribution can be as well inserted in the electronic problem:

$$\left[T_\theta + E_{el}(\theta)\right]\chi(\theta) = E\,\chi(\theta)$$

$$\boxed{\left[T_\pi + V_{\pi\text{-}ion} + V_{\pi\text{-}\pi} + V_{ion\text{-}ion}\right]\varphi = E_{el}\,\varphi}$$

*

The P-P-P Hamiltonian is a model H. for this electronic problem

P-P-P Hamiltonian (III)

- The next step is the LCAO approximation in the drastic limit of 1 p_z orbital per carbon atom:

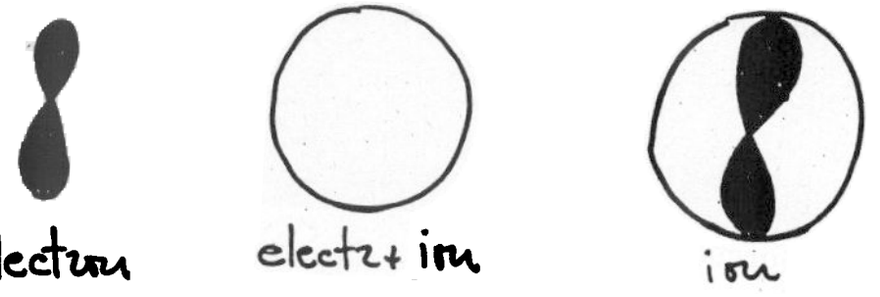
SINGLE PARTICLE HO $\rightarrow$ $\varphi_i(r) = \sum_\alpha c_{\alpha i}\, p_z(r - R_\alpha) \equiv \sum_\alpha c_{\alpha i}\, \varphi_\alpha(r)$

- The Hamiltonian for the many-electron problem (*) can be written in II quantiz.

$$H = \sum_{\alpha\alpha'} T_{\pi,\alpha\alpha'}\, \hat{c}^+_\alpha \hat{c}_{\alpha'} + V_{\pi\text{-ion},\alpha\alpha'}\, \hat{c}^+_\alpha \hat{c}_{\alpha'} +$$

$$+ \sum_{\alpha\beta\beta'\alpha'} V_{\pi\text{-}\pi,\alpha\beta\alpha'\beta'}\, \hat{c}^+_\alpha \hat{c}^+_\beta \hat{c}_{\beta'} \hat{c}_{\alpha'} + V_{\text{ion-ion}}$$

- Finally, in the same spirit of the <u>jellium</u> model, we take the ion as a hole with the same spatial simmetry of the electron:



P-P-P Hamiltonian (IV)

- More explicitly we can rewrite the Hamiltonian as:

$$H = \hat{T} + \hat{V}$$

where: ($\hat{T}$ is the kinetic term)

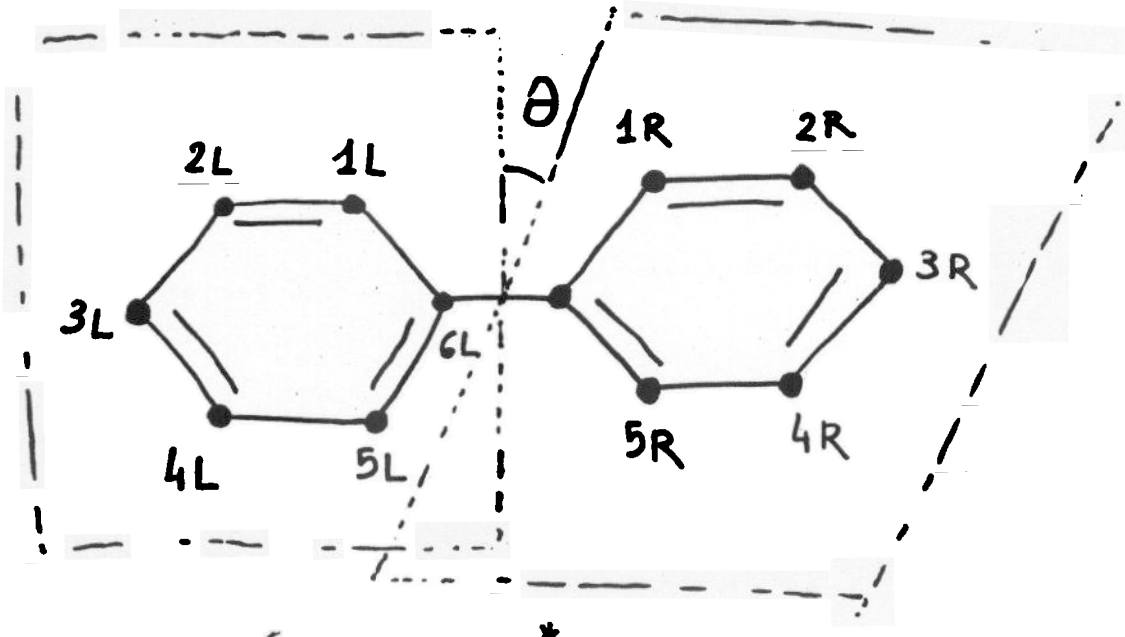
$$\hat{V} = \int dr_1 dr_2 \, \hat{\rho}(r_1) \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} \hat{\rho}(r_2)$$

$$\hat{\rho}(r) = \sum_{\alpha\beta\sigma} \left[\phi_\alpha^*(r - R_\alpha) \phi_\beta(r - R_\beta) - \frac{1}{12} \sum_\lambda |\phi_\beta(r - R_\lambda)|^2 \delta_{\alpha\beta} \right] \cdot \hat{c}^+_{\alpha\sigma} \hat{c}_{\beta\sigma}$$

- The definition of $\hat{V}$ includes in principle multicentered integrals. In the approximation of nearest two centers integrals we obtain the P-P-P Hamiltonian

$$H = t \sum_{\alpha+1\alpha\sigma} \left(\hat{c}^+_{\alpha\sigma} \hat{c}_{\alpha+1\sigma} + \hat{c}^+_{\alpha+1\sigma} \hat{c}_{\alpha\sigma} \right) + U \sum_\alpha \left(\hat{n}_{\alpha\uparrow} - \frac{1}{2} \right) \left(\hat{n}_{\alpha\downarrow} - \frac{1}{2} \right) + V \sum_{\langle \alpha < \beta \rangle} \left(\hat{n}_\alpha - 1 \right) \left(\hat{n}_\beta - 1 \right)$$

P-P-P Hamiltonian for BM



$$t_{LL} = t_{RR} = \int dr_1 dr_2 \frac{\phi_z^*(r_1)\phi_z(r_1+d)|\phi_z(r_2)|^2}{|r_1 - r_2|} \frac{e^2}{4\pi\varepsilon_0}$$

$$+ \int dr_1 \; \phi_z^*(r_1) \frac{(-\nabla^2)\hbar^2}{2m} \phi_z(r_1+d) \equiv b(d)$$

$$t_{6L6R} = b(d') \cos\theta$$

U and V are also defined in terms of the Coulomb integrals

$$U = \int dr_1 dr_2 \frac{e^2}{4\pi\varepsilon_0} \frac{|\phi_z(r_1)|^2 |\phi_z(r_2)|^2}{|r_1 - r_2|}$$

$$V = \int dr_1 dr_2 \frac{e^2}{4\pi\varepsilon_0} \frac{|\phi_z(r_1)|^2 |\phi_z(r_2+d)|^2}{|r_1 - r_2|}$$

Benzene

- We start considering the single particle hamiltonian of the benzene ring:

$$H_B^0 = \begin{bmatrix} 0 & b & 0 & 0 & 0 & b \\ b & 0 & b & 0 & 0 & 0 \\ 0 & b & 0 & b & 0 & 0 \\ 0 & 0 & b & 0 & b & 0 \\ 0 & 0 & 0 & b & 0 & b \\ b & 0 & 0 & 0 & b & 0 \end{bmatrix}$$

- In analogy with the Bloch theorem one can diagonalize this Hamiltonian in a basis ℓ of the quasi-angular momentum

$$c_\ell^+ = \frac{\sum_\alpha e^{i\ell \frac{\pi}{3}\alpha} c_\alpha^+}{\sqrt{6}}$$

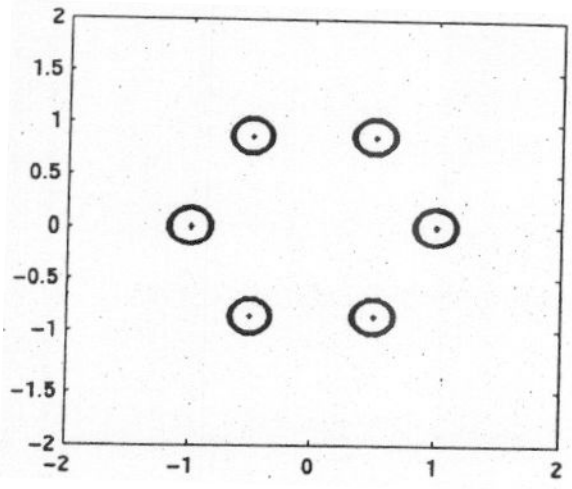
$$\ell = -2, -1, 0, 1, 2, 3 \qquad \varepsilon_\ell = +2b \cos\left(\frac{\pi}{3}\ell\right)$$

$|1\rangle$, $|-1\rangle$ are degenerate

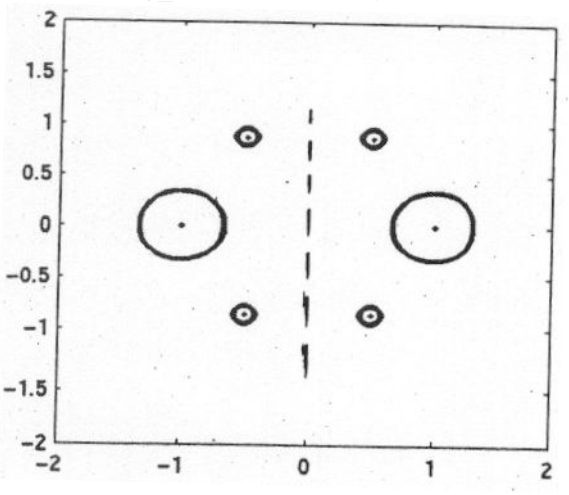
$|2\rangle$, $|-2\rangle$

MOLECULAR ORBITALS OF BENZENE

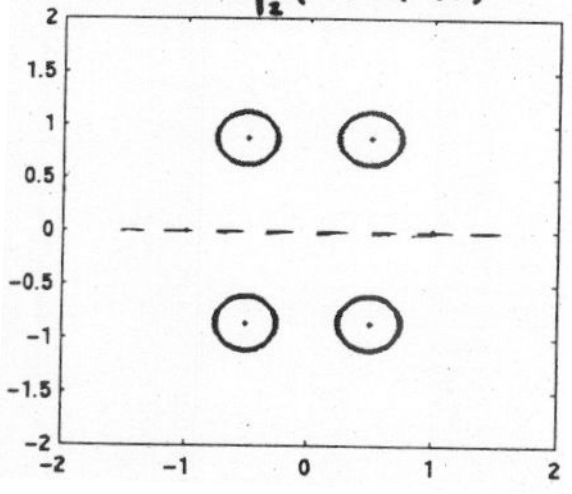
$|0\rangle$



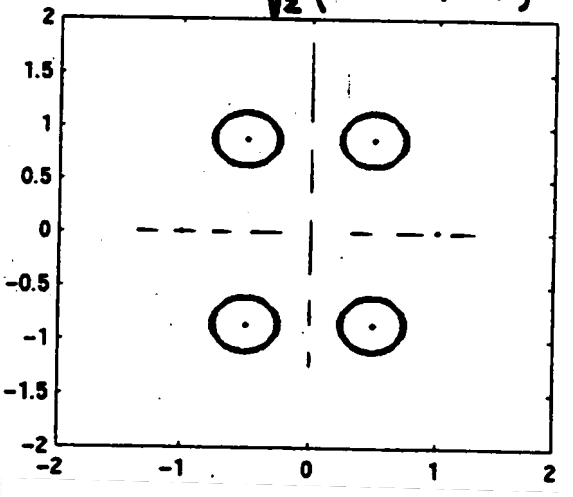
$|1+\rangle \equiv \frac{1}{\sqrt{2}}(|1\rangle + |-1\rangle)$



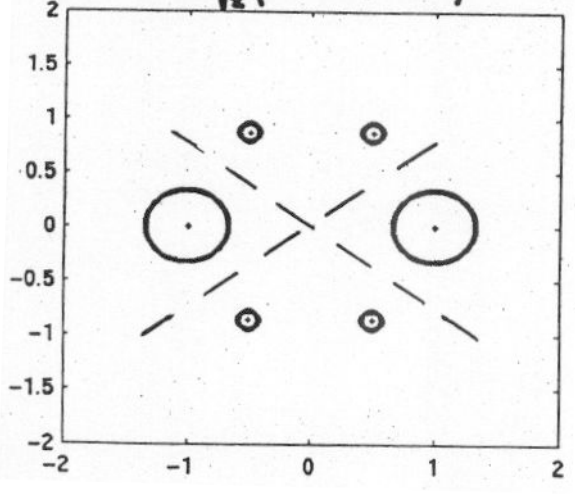
$|1-\rangle \equiv \frac{1}{\sqrt{2}}(|1\rangle - |-1\rangle)$



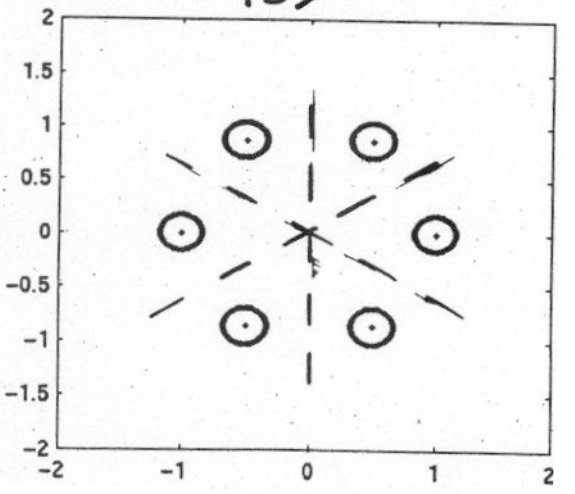
$|2-\rangle \equiv \frac{1}{\sqrt{2}}(|2\rangle - |-2\rangle)$



$|2+\rangle \equiv \frac{1}{\sqrt{2}}(|2\rangle + |-2\rangle)$



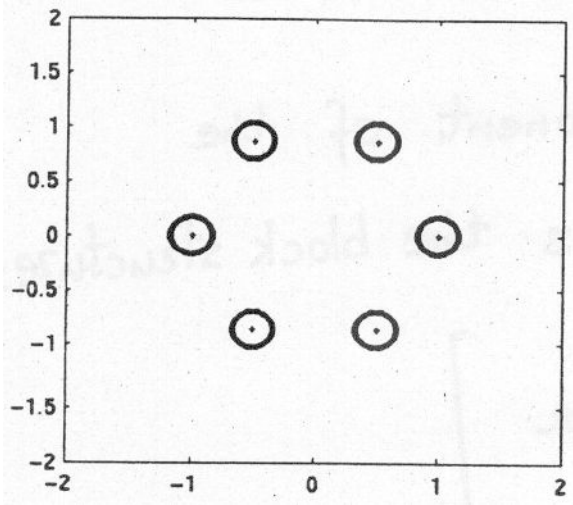
$|3\rangle$



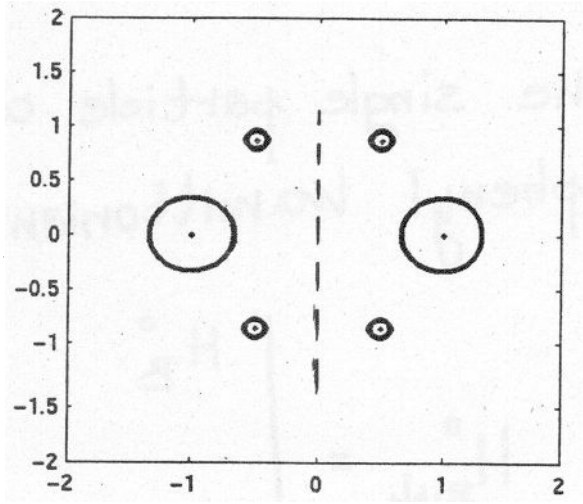
The pseudo-angular momentum ℓ counts the # of NODES.

MOLECULAR ORBITALS OF BENZENE

$|0\rangle$



$|1+\rangle \equiv \frac{1}{\sqrt{2}}(|1\rangle + |-1\rangle)$



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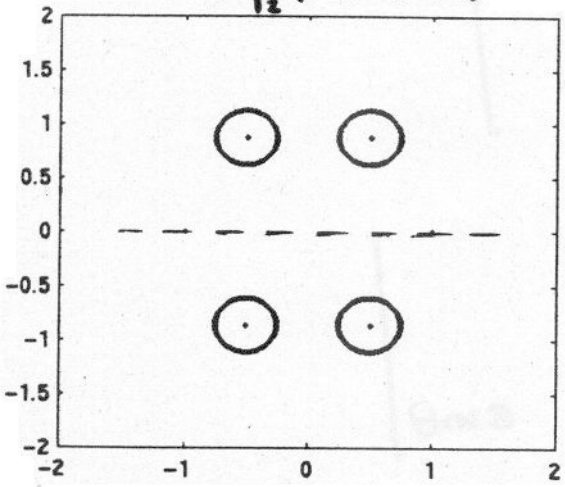
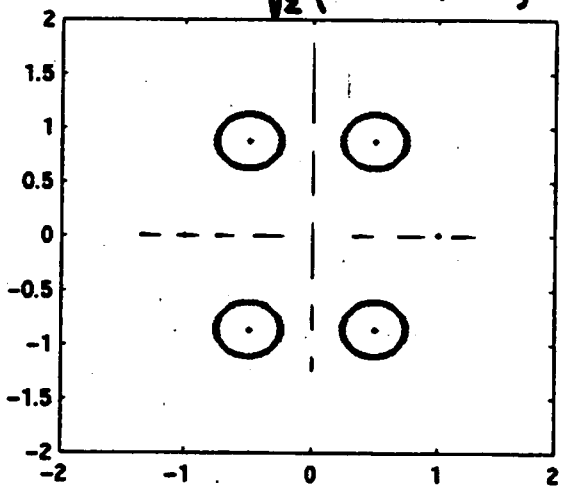
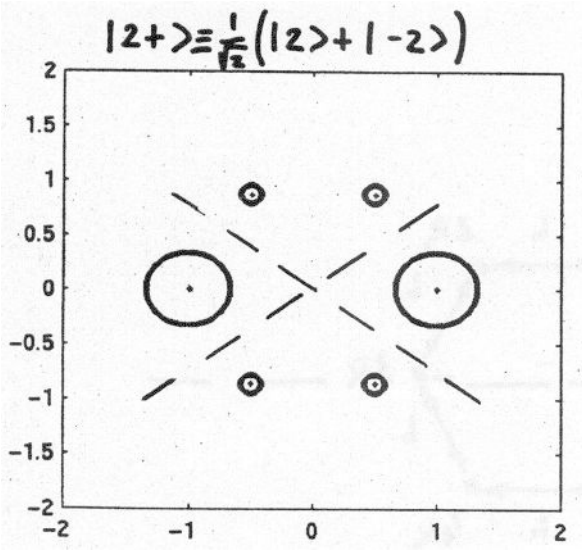


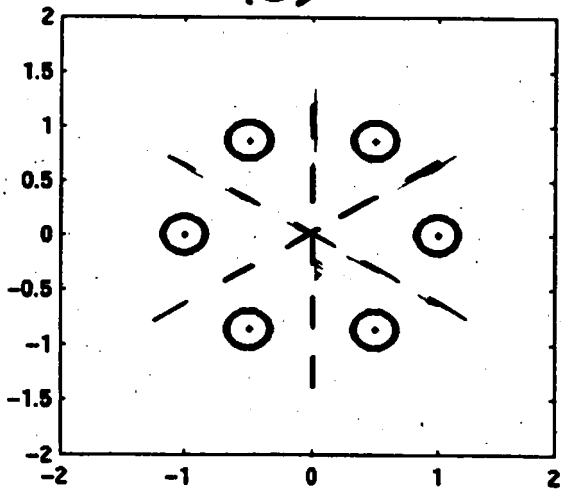
$|2-\rangle \equiv \frac{1}{\sqrt{2}}(|2\rangle - |-2\rangle)$



$|2+\rangle \equiv \frac{1}{\sqrt{2}}(|2\rangle + |-2\rangle)$



$|3\rangle$



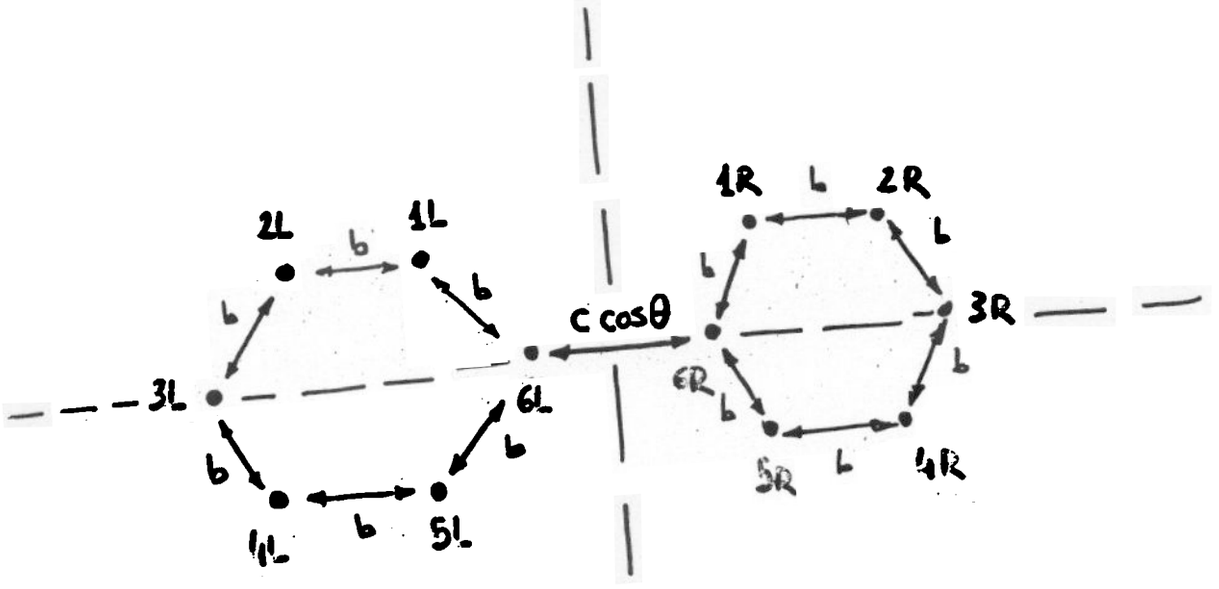
The pseudo-angular momentum ℓ counts the # of NODES.

NON-INTERACTING BIPHENYL

- The single particle component of the biphenyl hamiltonian has the block structure:

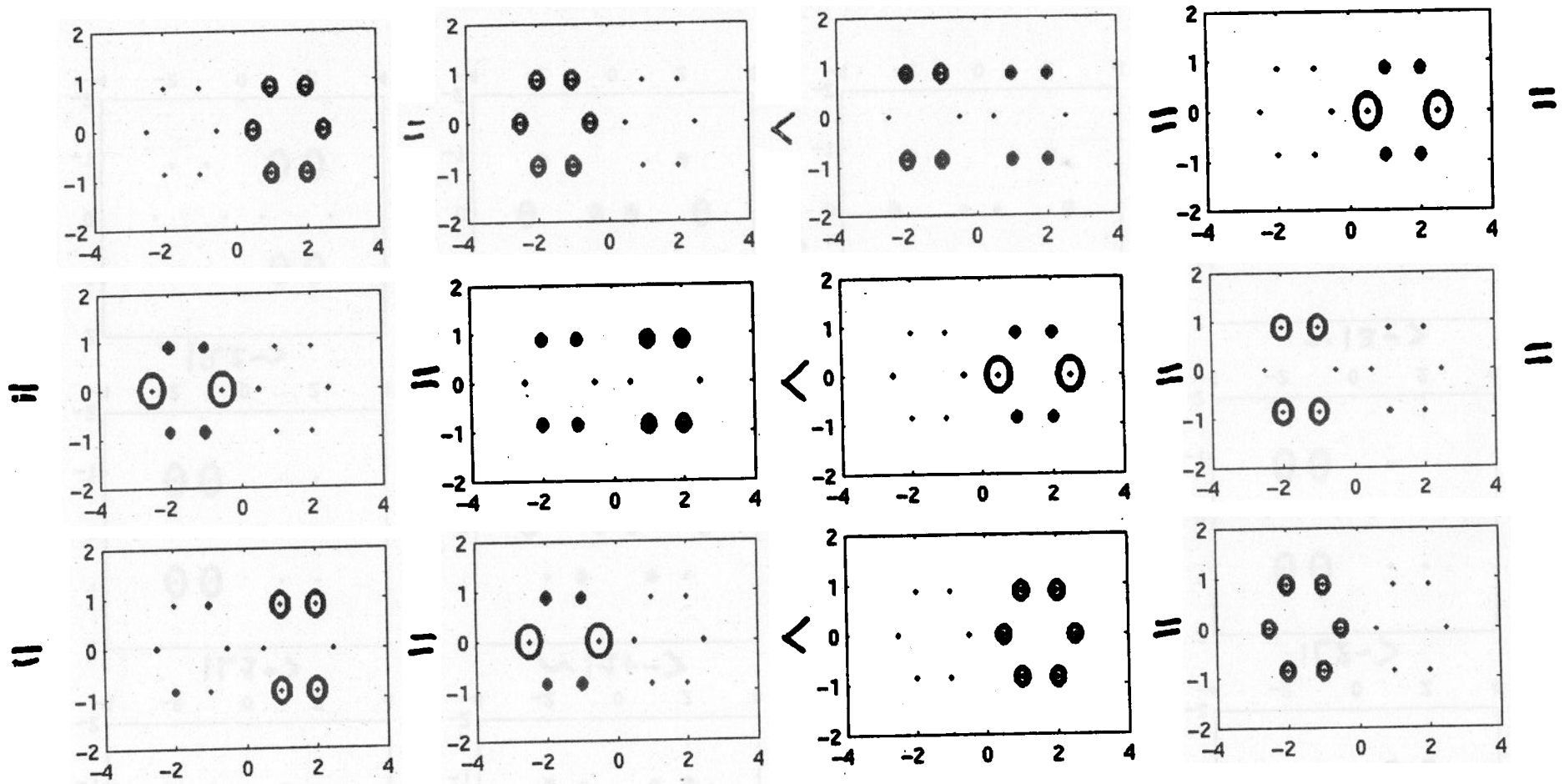
$$H^{o}_{Biph} = \begin{bmatrix} H^{o}_{B} & T_{LR} \\ T_{RL} & H^{o}_{B} \end{bmatrix}$$

where $T_{LR} = T_{RL}^{+} = \begin{bmatrix} & \\ & c\cos\theta \end{bmatrix}$

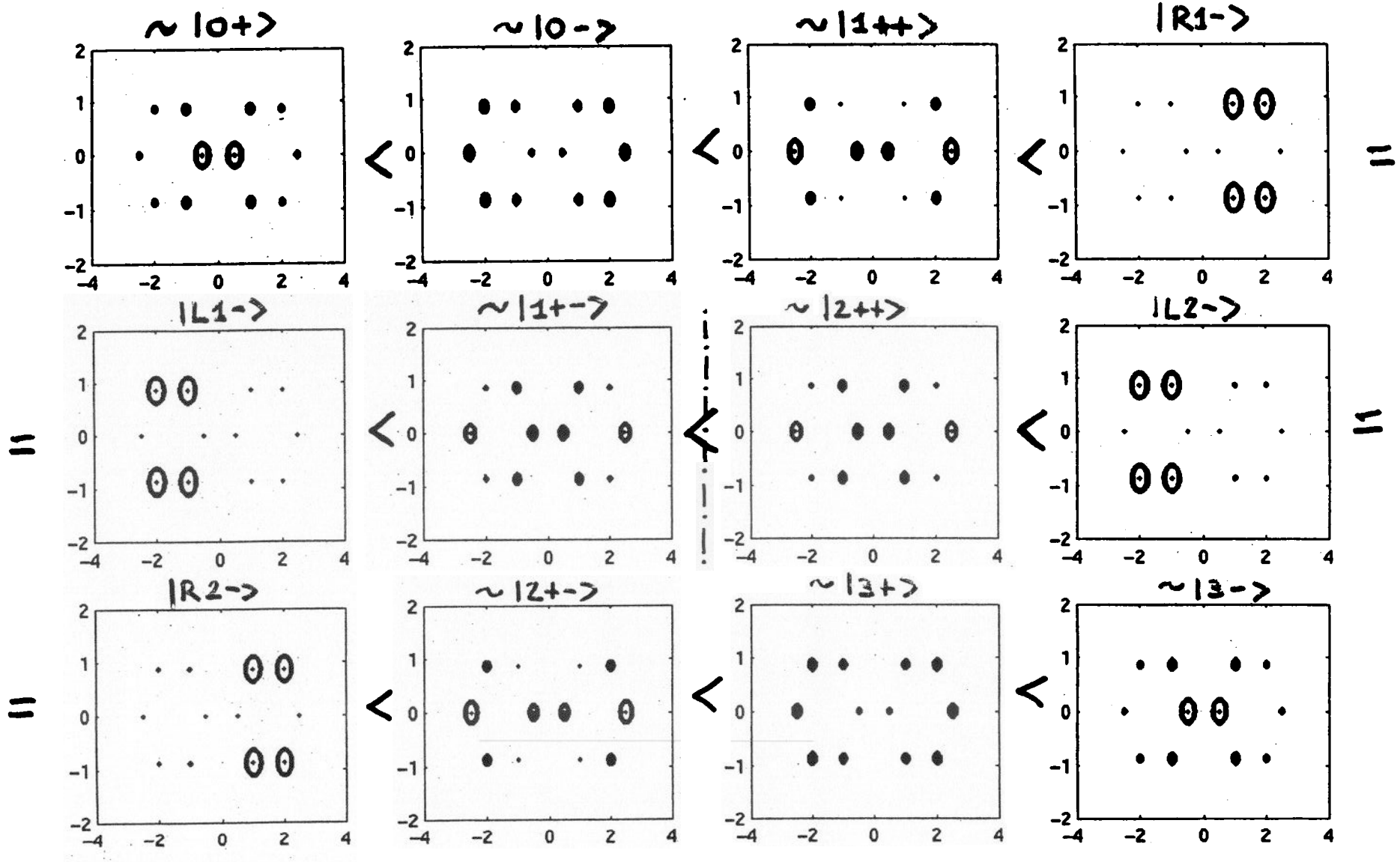


THE SYMMETRIES OF THE MOLECULE

BIPHENYL EIGENVECTORS $\theta = \pi/2$



BIPHENYL EIGENVECTORS $\theta = 0$



Eigenvalues of $H^{\circ}_{Biph.}$ (1)

- Taking advantage of the symmetries of the molecule we rewrite the Hamiltonian in the basis

$$\frac{1}{2}[|2L\rangle - |4L\rangle + |2R\rangle - |4R\rangle]$$
$$\frac{1}{2}[|1L\rangle - |5L\rangle + |1R\rangle - |5R\rangle]$$

} up-down antisimm

$$\frac{1}{\sqrt{2}}[|3L\rangle + |3R\rangle]$$
$$\frac{1}{2}[|2L\rangle + |4L\rangle + |2R\rangle + |4R\rangle]$$
$$\frac{1}{2}[|1L\rangle + |5L\rangle + |1R\rangle + |5R\rangle]$$

} up-down simm

$$\frac{1}{\sqrt{2}}[|6L\rangle - |6R\rangle]$$

$\vdots$

] L-R SIMMETRIC

and the correspondent L-R antisimmetric

The Hamiltonian H°_{Biph} acquires the diagonal block structure

$$H^{\circ}_{Biph} = \begin{bmatrix} \begin{matrix} 0 & b \\ b & 0 \end{matrix} & & & \\ & M_1 & & \\ & & \begin{matrix} 0 & b \\ b & 0 \end{matrix} & \\ & & & M \end{bmatrix}$$

(4 × 4 blocks)

Eigenvalues of H°_{Biph} (II)

- The up-down antisimmetric blocks are easily diagonalized and give the eigenvalues:

$$b \times 2 \quad \leftrightarrow \quad |2-+\rangle \text{ and } |1--\rangle$$
$$-b \times 2 \quad \leftrightarrow \quad |2-+\rangle \text{ and } |2--\rangle$$

- The M_1 and M_2 blocks have characteristic polinomials:

$$x^4 \pm cx^3 \cos\varphi - 5b^2x^2 \mp 3b^2cx\cos\varphi + 4b^4$$

We find the approximate roots by the ansatz:

$$x_i = x_{i0} + x_{i1}\cos\varphi + x_{i2}(\cos\varphi + 1)$$

and $x_{ij}/x_{ij+1} = k^{-1} \gg 1$

I obtain a set of recursive equations for the coefficients x_{ij}.

Eigenvalues of H'_{Bip} (III)

■ The approximate solutions read:

$$x_{0+} = 2b + \frac{c}{6}\cos\varphi + \frac{35}{864}\frac{c^2}{b}(\cos 2\varphi + 1)$$
$$x_{1+} = b + \frac{c}{3}\cos\varphi + \frac{1}{108}\frac{c^2}{b}(\cos 2\varphi + 1)$$
$$x_{2+} = -b + \frac{c}{3}\cos\varphi - \frac{1}{108}\frac{c^2}{b}(\cos 2\varphi + 1)$$
$$x_{3+} = -2b + \frac{c}{6}\cos\varphi - \frac{35}{864}\frac{c^2}{b}(\cos 2\varphi + 1)$$

} Simmetric LR

$$x_{0-} = 2b - \frac{c}{6}\cos\varphi + \frac{35}{864}\frac{c^2}{b}(\cos 2\varphi + 1)$$
$$x_{1-} = b - \frac{c}{3}\cos\varphi + \frac{1}{108}\frac{c^2}{b}(\cos 2\varphi + 1)$$
$$x_{2-} = b - \frac{c}{3}\cos\varphi - \frac{1}{108}\frac{c^2}{b}(\cos 2\varphi + 1)$$
$$x_{3-} = -2b - \frac{c}{6}\cos\varphi - \frac{35}{864}\frac{c^2}{b}(\cos 2\varphi + 1)$$

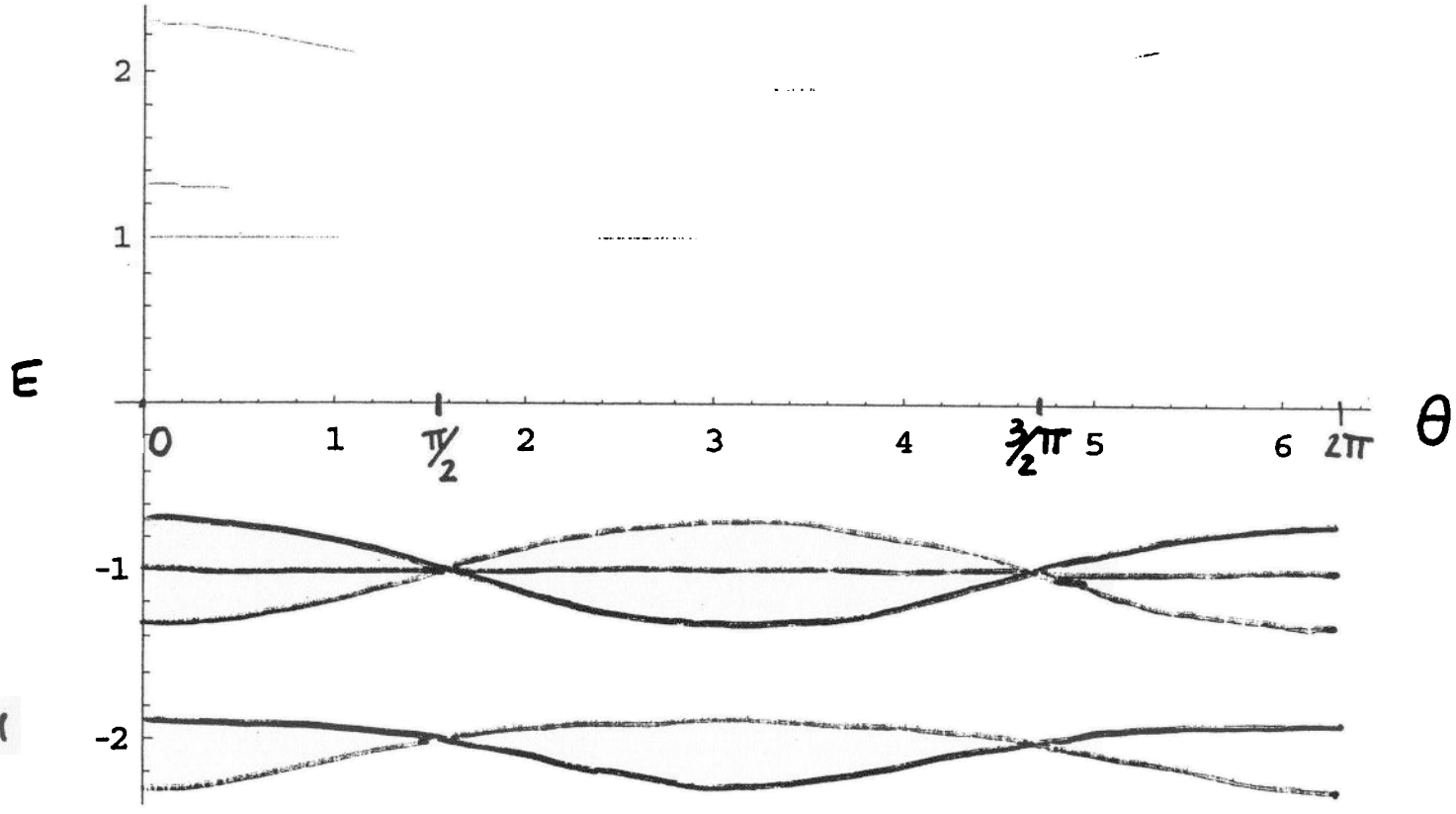
} Antisimmetric LR

$$\boxed{E_{conj}(\theta) = 4b\left[4 + \frac{43}{432}\frac{c^2}{b^2}\cos^2\theta\right]}$$

■ The "electronic" potential energy $E_{conj}(\theta)$ has 2 minima: $\theta = 0$, $\theta = \pi$.
In this configuration the π-electrons are maximally delocalized.

Diphenyl Eigenvalues

.b = -1

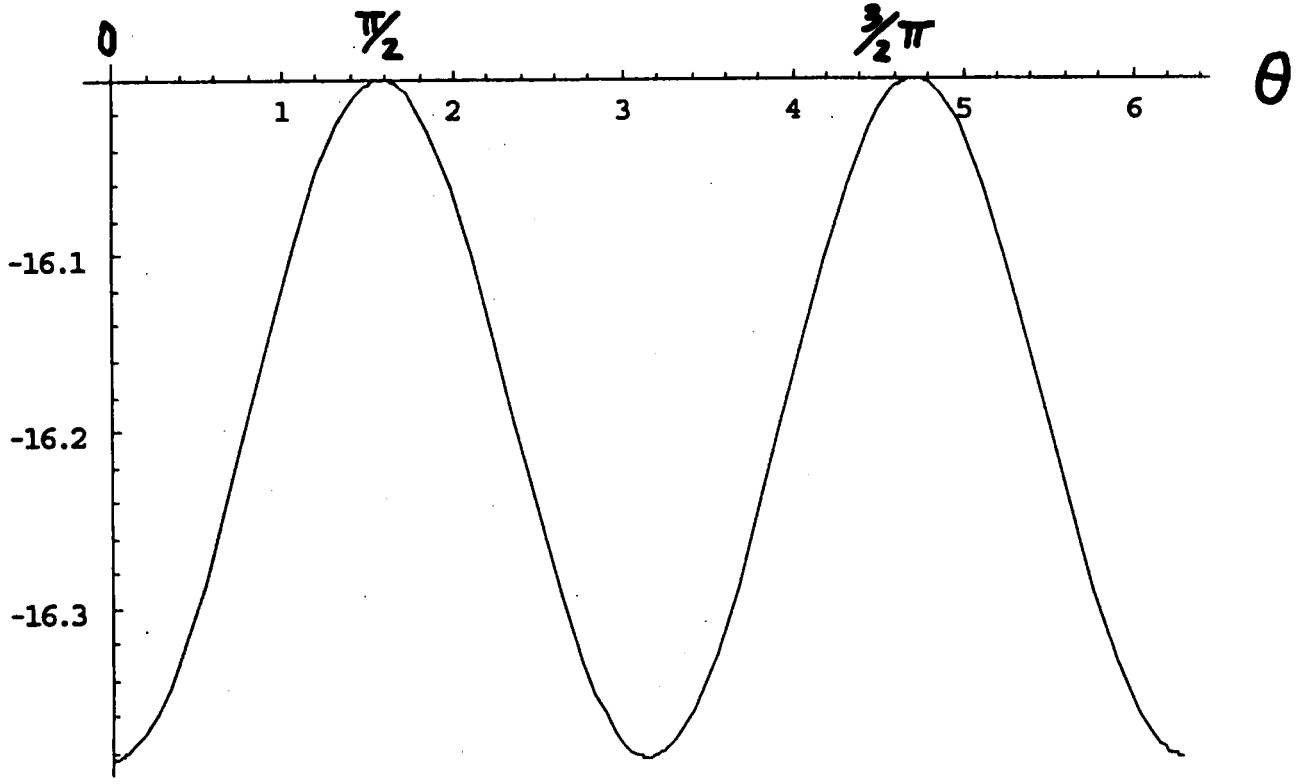


L-R ASIMM

L-R SIMM

Conjugation Energy for Diphenyl

$b = -1$



CONJUGATION ENERGY AT $\theta = \pi/2, 3/2\pi = 2\,[\underbrace{2b + 2b}_{L} + \underbrace{2b + 2b}_{R}] = 16\,b$

$|L1\pm\rangle$ $|L0\rangle$ $|R1\pm\rangle$ $|R0\rangle$

2 ← spin

Steric Repulsion

- The ab initio calculation shows that the neutral BM tends to avoid also the planar configurations: $\theta = 0$, $\theta = \pi$.

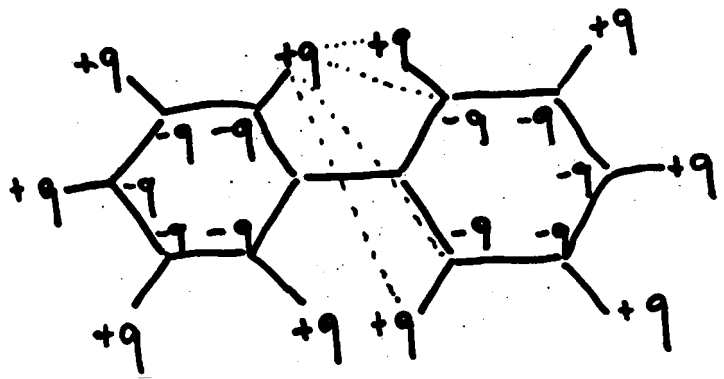
This is due to the STERIC REPULSION:

- ELECTROSTATIC INTERACTION
- EXCHANGE REPULSION

- Every tight binding model at half filling exhibits uniform (1) electron density

  ⇒ The Hartree component of the interaction Hamiltonian vanishes (α is at least θ indep)

A residual electrostatic interaction derives from the POLARIZED CH BONDS



→

■ The residual electrostatic interaction

* HAS THE CORRECT SIMMETRY

ex. H-H

$$V_{H\text{-}H}(\theta) = \frac{q^2 c^2}{4\pi\varepsilon_0}\frac{2}{\ell_1}\left[\frac{1}{a} + \frac{1}{\sqrt{1+a^2\sin^2\frac{\theta}{2}}} + \frac{1}{\sqrt{1+a^2\cos^2\frac{\theta}{2}}}\right]$$

ℓ_1, a geometrical factor.

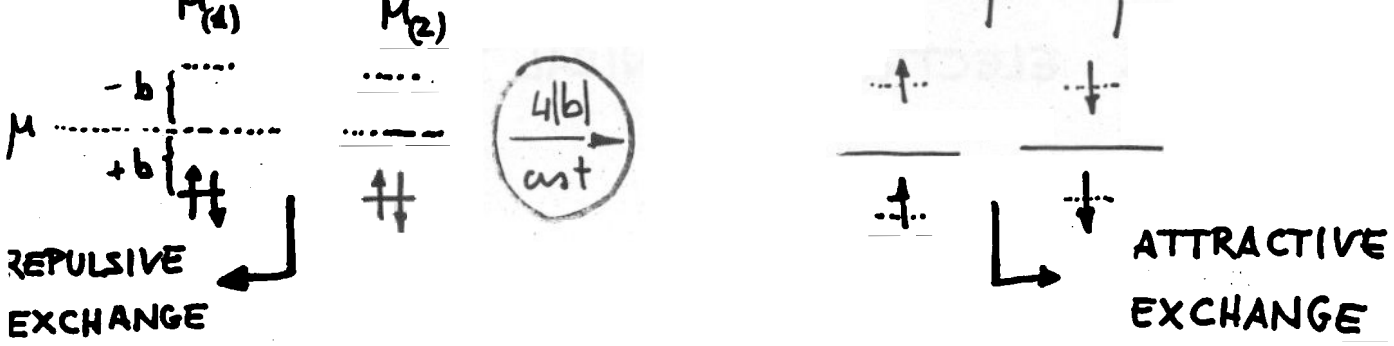
* THE POLARIZATION REQUIRED TO FIT THE ab initio CALCULATION IS UNPHYSICAL

$$q_{fit} \sim 5\, q_{theo}$$

■ The sign of the exchange interaction

■ H_2: Exchange interaction reduces the Coulomb repulsion:

■ M_2: Exchange interaction can change sign: !



(Still a lot) TO DO

- Insert the exchange interaction and extract b, c, U, V From a fitting to the ab initio potential

- Within the same model evaluate the $Biph^-$ potential

- Insert:
  * Coupling to electrical lead
  * Coupling to dissip. mech. bath

DISCUSS ELECTRO MECHANICAL PROPERTIES