Handouts - Download and Read!

http://www.chem.tamu.edu/rgroup/hughbanks/courses/673/handouts/handouts.html

- ★ translation_groups2.pdf
- ★ translation_groups3.pdf
- ★ transitions.pdf   Provides background for selection rules. You do not need to memorize the derivation, but results in "boxes" are important to know!

Complex Numbers; Digression

- ★ Cartesian Forms
- ★ The complex plane, vector forms
- ★ polar representation of complex numbers and vectors

Cyclic Groups

Consider C_N, the cyclic group consisting of the operations C_N, C_N^2, C_N^3, ..., $C_N^{N\text{-}1}$, C_N^N $= E$. Because all the operations are in the different classes, there are N irreducible representations and they are all one dimensional. This means that the characters are the same as the matrices - just numbers.

Character Tables for Cyclic Groups

$\varepsilon = \exp(2\pi i / N)$

	C_N	$C_N^{\mathbf{2}}$	$C_N^{\mathbf{3}}$	$\cdots$	$C_N^{\mathbf{N-1}}$	$C_N^{\mathbf{N}} = E$
Γ^1	ε	ε^2	ε^3	$\cdots$	ε^{N-1}	ε^N
Γ^2	ε^2	ε^4	ε^6	$\cdots$	ε^{2N-2}	ε^{2N}
Γ^3	ε^3	ε^6	ε^9	$\cdots$	ε^{3N-3}	ε^{3N}
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\vdots$
Γ^{N-1}	ε^{N-1}	ε^{2N-2}	ε^{3N-3}	$\cdots$	ε^{-2}	$\varepsilon^{N(N-1)}$
Γ^N	ε^N	ε^{2N}	ε^{3N}	$\cdots$	ε^{-1}	ε^{N^2}

Example

- ★ Use the C_6 group to find the characters of the reducible representation obtained using the 6 carbon pπ orbitals of benzene as a basis — then find the irred. reps. spanned by this rep.
- ★ Draw the complex coefficients of the orbitals for each irreducible representation.
- ★ Draw real counterparts of these orbitals.

C_6 Group

$\varepsilon = \exp(2\pi i/6)$

C_6	C_6	C_6^{2}	C_6^{3}	C_6^{4}	C_6^{5}	$C_N^{6} = E$
Γ^1	ε	ε^2	ε^3	ε^4	ε^5	ε^6
Γ^2	ε^2	ε^4	ε^6	ε^8	ε^{10}	ε^{12}
Γ^3	ε^3	ε^6	ε^9	ε^{12}	ε^{15}	ε^{18}
Γ^4	ε^4	ε^8	ε^{12}	ε^{16}	ε^{20}	ε^{24}
Γ^5	ε^5	ε^{10}	ε^{15}	ε^{20}	ε^{25}	ε^{30}
Γ^6	ε^6	ε^{12}	ε^{18}	ε^{24}	ε^{30}	ε^{36}

C_6	E	C_6	C_6^{2}	C_6^{3}	C_6^{4}	C_N^{5}
$\Gamma^0 = \Gamma^6$	1	1	1	1	1	1
Γ^1	1	ε	ε^2	ε^3	ε^4	ε^5
Γ^2	1	ε^2	ε^4	ε^6	ε^8	ε^{10}
Γ^3	1	ε^3	ε^6	ε^9	ε^{12}	ε^{15}
Γ^4	1	ε^4	ε^8	ε^{12}	ε^{16}	ε^{20}
Γ^5	1	ε^5	ε^{10}	ε^{15}	ε^{20}	ε^{25}

$\varepsilon = \exp(2\pi i/6)$

C_6	E	C_6	C_6^2	C_6^3	C_6^4	C_6^5
$\Gamma^0 = \Gamma^6$	1	1	1	1	1	1
Γ^1	1	ε	ε^2	ε^3	ε^4	ε^5
Γ^2	1	ε^2	ε^4	ε^6	ε^8	ε^{10}
Γ^3	1	ε^3	ε^6	ε^9	ε^{12}	ε^{15}
Γ^4	1	ε^4	ε^8	ε^{12}	ε^{16}	ε^{20}
Γ^5	1	ε^5	ε^{10}	ε^{15}	ε^{20}	ε^{25}

Let ψ_1 be a basis function that belongs to Γ^1, then

$$C_6\psi_1 = \varepsilon\psi_1,\ C_6^2\psi_1 = \varepsilon^2\psi_1,\ \cdots,\ C_6^5\psi_1 = \varepsilon^5\psi_1$$

Write ψ_1 as a combination of $p\pi$ basis functions,

$$\psi_1 = \phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6$$

$$C_6\psi_1 = C_6\left(\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6\right) = \varepsilon\psi_1$$

$$\phi_2 + c_2\phi_3 + c_3\phi_4 + c_4\phi_5 + c_5\phi_6 + c_6\phi_1 = \varepsilon\phi_1 + c_2\varepsilon\phi_2 + c_3\varepsilon\phi_3 + c_4\varepsilon\phi_4 + c_5\varepsilon\phi_5 + c_6\varepsilon\phi_6$$

$$c_2\varepsilon = 1 \quad \Rightarrow \quad c_2 = \varepsilon^* = \varepsilon^{-1}$$

$$c_2 = \varepsilon^{-1} = c_3\varepsilon \quad \Rightarrow \quad c_3 = \varepsilon^{-2}$$

$\varepsilon = \exp(2\pi i/6)$

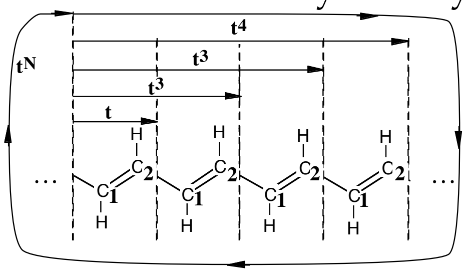
C_6	E	C_6	C_6^{2}	C_6^{3}	C_6^{4}	C_6^{5}
$\Gamma^0 = \Gamma^6$	1	1	1	1	1	1
$\Gamma^1 = E_1$	1	ε	ε^2	-1	$-\varepsilon$	$-\varepsilon^2$
$\Gamma^2 = E_2$	1	ε^2	$-\varepsilon$	1	ε^2	$-\varepsilon$
$\Gamma^3 = B$	1	-1	1	-1	1	-1
$\Gamma^4 = E_2$	1	$\varepsilon^2{}^*$	$-\varepsilon^*$	1	$\varepsilon^2{}^*$	$-\varepsilon^*$
$\Gamma^5 = E_1$	1	ε^*	$\varepsilon^2{}^*$	-1	$-\varepsilon^*$	$-\varepsilon^2{}^*$

Make the identification with chaacter tables in some books:

$$\varepsilon^3 = \varepsilon^9 = \varepsilon^{15} = \varepsilon^{21} = -1,\ \varepsilon^6 = \varepsilon^{12} = \varepsilon^{18} = \varepsilon^{24} = 1$$

Translation Group (1-dimension)

★ The one-dimensional translation group is just a particular cyclic group of order N. The trans-polyacetylene below is an example of a system with translational symmetry.



1-D Translation Group Char. Table

This has the same appearance as the C_N group's character table:

$\varepsilon = \exp(2\pi i / N)$

	t	$\mathbf{t^2}$	$\mathbf{t^3}$	$\cdots$	$\mathbf{t^{N-1}}$	$\mathbf{t^N} = E$
Γ^1	ε	ε^2	ε^3	$\cdots$	ε^{N-1}	ε^N
Γ^2	ε^2	ε^4	ε^6	$\cdots$	ε^{2N-2}	ε^{2N}
Γ^3	ε^3	ε^6	ε^9	$\cdots$	ε^{3N-3}	ε^{3N}
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\vdots$
Γ^{N-1}	ε^{N-1}	ε^{2N-2}	ε^{3N-3}	$\cdots$	$\varepsilon^{(N-1)^2}$	$\varepsilon^{N(N-1)}$
Γ^N	ε^N	ε^{2N}	ε^{3N}	$\cdots$	$\varepsilon^{N(N-1)}$	ε^{N^2}

1-D Translation Group Char. Table - Rearranged

$\varepsilon = \exp(2\pi i / N)$

$\mathbf{T_N}$	E	**t**	$\mathbf{t^2}$	$\cdots$	$\mathbf{t^{N-2}}$	$\mathbf{t^{N-1}}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\vdots$
$\Gamma^{-N/2}$	1	-1	1	$\cdots$	1	-1
$\Gamma^{-N/2+1}$	1	$-\varepsilon$	ε^2	$\cdots$	ε^{-2}	$-\varepsilon^{-1}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\vdots$
Γ^{-1}	1	ε^{-1}	ε^{-2}	$\cdots$	$\varepsilon^{-(N-2)}$	$\varepsilon^{-(N-1)}$
Γ^0	1	1	1	$\cdots$	1	1
Γ^1	1	ε^1	ε^2	$\cdots$	ε^{N-2}	ε^{N-1}
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\vdots$
$\Gamma^{N/2}$	1	-1	1	$\cdots$	1	-1
$\Gamma^{N/2+1}$	1	$-\varepsilon$	ε^2	$\cdots$	ε^{-2}	$-\varepsilon^{-1}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

Character Table for $\boldsymbol{T}_N$, rewritten

★ All the IRs of $\boldsymbol{T}_N$ have the form:

$\varepsilon = e^{2\pi i/N}$	**t**	$\mathbf{t^2}$	$\mathbf{t^3}$	$\cdots$	$\mathbf{t^{N-1}}$	$\mathbf{t^N} = E$
Γ^j	ε^j	ε^{2j}	ε^{3j}	$\cdots$	ε^{-j}	1

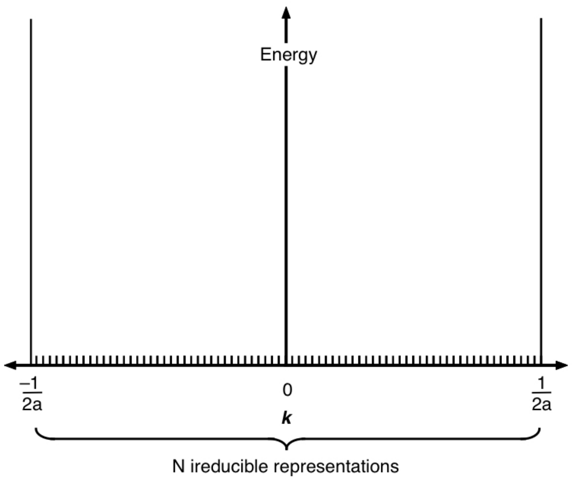
$-N/2+1 < j < N/2$

We make the substitution $k = \left(\frac{1}{a}\right) \times \left(\frac{j}{N}\right)$; where $-\frac{1}{2a} < k \le \frac{1}{2a}$

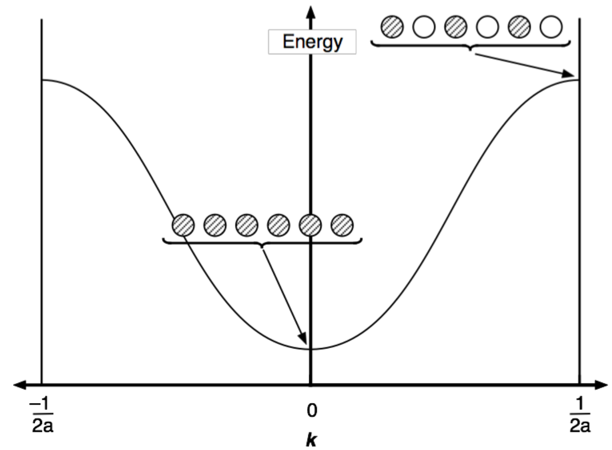
Making the substitution, $\varepsilon^j = (e^{2\pi i/N})^j = e^{2\pi i k a}$. This is rewritten to yield

	E	**t**	$\mathbf{t^2}$	$\mathbf{t^3}$	$\cdots$	$\mathbf{t^{N-1}}$
$\Gamma(k)$	1	$e^{2\pi i(k\bullet a)}$	$e^{2\pi i(k\bullet 2a)}$	$e^{2\pi i(k\bullet 3a)}$	$\cdots$	$e^{-2\pi i(k\bullet a)}$

1-D Energy Level Diagram



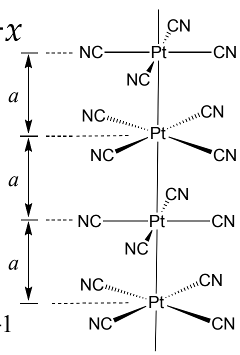
1-D s-band Dispersion curve



Examples

- ★ Find the characters of the reducible representation obtained using the N hydrogen 1*s* orbitals of a hypothetical H-atom chain (with N atoms) as a basis — then find the irreducible reps. spanned by this rep.
- ★ Follow the same procedure (*i*) using the longitudinal stretching vectors as a basis, (*ii*) using the transverse stretching vectors as a basis, (*iii*) using p_σ orbitals as a basis.

$[Pt(CN)_4]^{-2+x}$



Chains in $K_2[Pt(CN)_4]$ and $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$

$[Pt(CN)_4]^{-2}$: d(Pt-Pt) = a = 3.48 Å

$[Pt(CN)_4]^{-1.7}$: d(Pt-Pt) = a = 2.88 Å

$\alpha_p - \alpha_d = 8|\beta| \quad ; \quad \beta = -1$

$\beta_{dd} = \beta \qquad \beta_{pp} = 2\beta \qquad \beta_{dp} = 1.5\beta$

The tetracyanoplatinates crystallize such that square planar $Pt(CN)_4^{x-2}$ species stack upon each other as indicated in the illustration below. (Steric factors cause the square planar ions to stack in a staggered fashion, but *we'll proceed as if the stacking is eclipsed*, i.e., as if there is just one $Pt(CN)_4^{x-}$ ion per unit cell.) Pt-Pt distances are markedly shortened (from 3.48 Å to 2.88 Å) when the platinum is oxidized by reaction with Br_2 – that results in the intercalation of some additional bromide ions (Br^-) into voids between the chains in the solid state structure.

$[Pt(CN)_4]^{-2+x}$

Consider only the largest Pt-Pt σ overlaps involving the $5d_{z^2}$ orbital (*occupied* for this d^8 complex) and the $6p_z$ orbital (a high-lying *unoccupied* orbital that is stabilized to some extent by overlap with the CN π* orbitals).

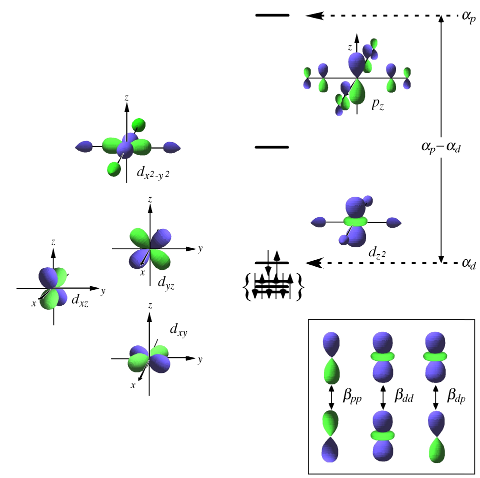
Set up the 2 × 2 k-dependent Hückel-like secular equation and solve it to obtain analytical k-dependent expressions for each of the two band curves. Draw a one-dimensional band dispersion diagram that includes bands that derive from the $5d_{z^2}$ and the $6p_z$ orbitals. Use these parameters:

$$\alpha_p - \alpha_d = 8|\beta| \quad ; \quad \beta = -1$$

$$\beta_{dd} = \beta \qquad \beta_{pp} = 2\beta \qquad \beta_{dp} = 1.5\beta$$

Mark the Fermi levels for both systems. Explain why the Pt-Pt distances shrink upon oxidation. Show the lowest energy allowed optical transitions for both systems.

$[Pt(CN)_4]^{-2+x}$



$$\begin{vmatrix} \alpha_d + (e^{2\pi i k \cdot a} + e^{2\pi i k \cdot -a})\beta - E & e^{2\pi i k \cdot a}(-1.5\beta) + e^{2\pi i k \cdot -a}(1.5\beta) \\ e^{2\pi i k \cdot -a}(-1.5\beta) + e^{2\pi i k \cdot a}(1.5\beta) & \alpha_p + (e^{2\pi i k \cdot a} + e^{2\pi i k \cdot -a})(-2\beta) - E \end{vmatrix} = 0$$

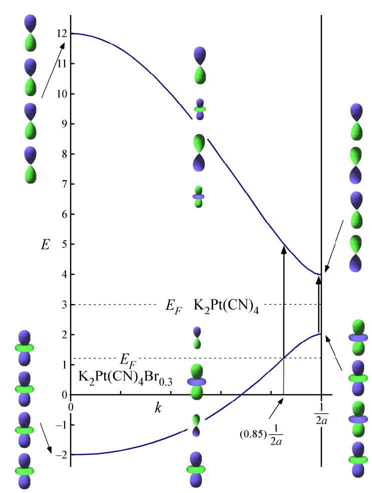
$$\begin{vmatrix} 2\beta\cos 2\pi ka - E & -3i\beta\sin 2\pi ka \\ 3i\beta\sin 2\pi ka & -8\beta - 4\beta\cos 2\pi ka - E \end{vmatrix} = 0$$

for convenience let $\beta = -1$

$$\begin{vmatrix} -2\cos 2\pi ka - E & 3i\sin 2\pi ka \\ -3i\sin 2\pi ka & 8 + 4\cos 2\pi ka - E \end{vmatrix} = 0$$

$$(E + 2\cos 2\pi ka)[E - (8 + 4\cos 2\pi ka)] - 9\sin^2 2\pi ka = 0$$

$$E = 4 + \cos 2\pi ka \pm \sqrt{25 + 24\cos 2\pi ka}$$



$[Pt(CN)_4]^{-2+x}$

2-dimensional Layers

✿ Bloch's Theorem in 2– or 3–D

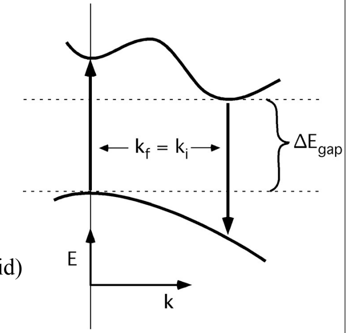
$$\varphi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{2\pi i \mathbf{k}\cdot\mathbf{R}}\varphi_{\mathbf{k}}(\mathbf{r}) \qquad \mathbf{R} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

$$\mathbf{k} = k_a\mathbf{a}^* + k_a\mathbf{b}^* + k_a\mathbf{c}^*$$

$$\mathbf{k}\cdot\mathbf{R} = k_a u + k_b v + k_c w$$

- Orbitals and bands for a square net of Hydrogen atoms
- Orbitals and bands for graphite

Selection Rules for Crystals: Vertical Transitions



Intensity, I $\propto \left[\int \psi_i^* \mathcal{H}'(t)\psi_f \, d\tau\right]^2$

where $\mathcal{H}'(t)$ is the perturbation of the molecule (solid) caused by the electric field of the radiation, and the electromagnetic wave propagating in the z-direction

$$\mathcal{H}'(t) = -\frac{E_x^0}{2}\sum_i q_i x_i \left\{ e^{2\pi i k_{photon} z_i} e^{-i\omega t} + e^{-2\pi i k_{photon} z_i} e^{i\omega t} \right\}$$

(See Eqs. 16 & 17 in Handout on "Transitions Between Stationary States")

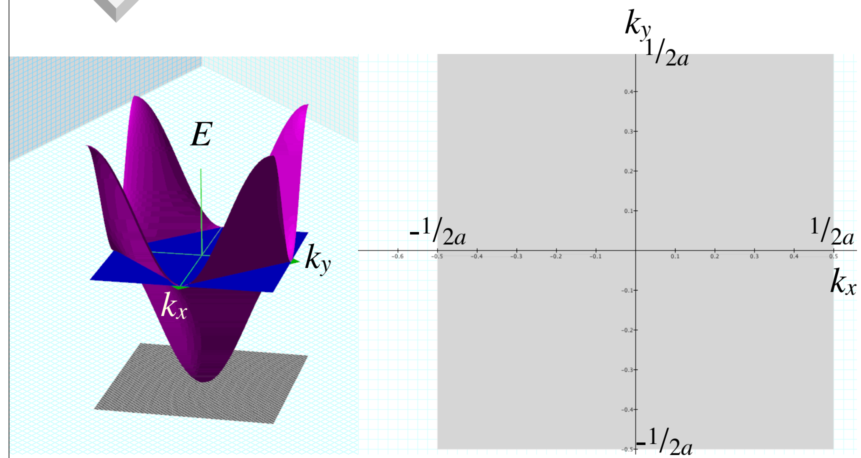
$\psi_i \propto u_{\mathbf{k}}(\mathbf{r}) e^{2\pi i \mathbf{k}_i \bullet \mathbf{r}}$ Important terms to consider ~ $\int e^{i\omega t} e^{2\pi i(\mathbf{k}_f - \mathbf{k}_i + \mathbf{k}_{photon})\bullet \mathbf{r}} d\tau$

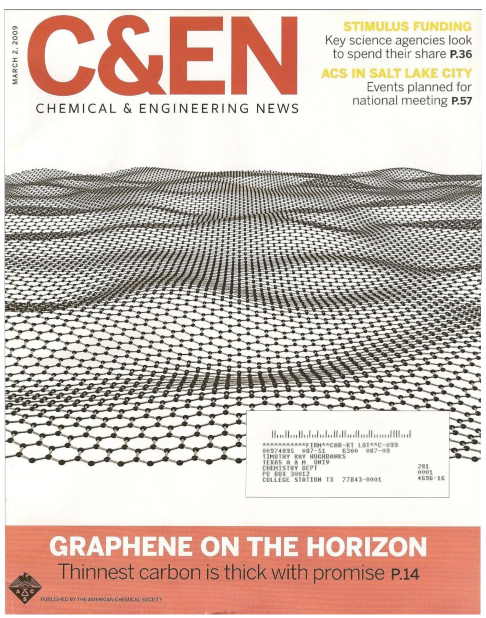
$\psi_f \propto u_{\mathbf{k}}(\mathbf{r}) e^{2\pi i \mathbf{k}_f \bullet r}$ I $= 0$ unless $\boxed{\mathbf{k}_f - \mathbf{k}_i + \mathbf{k}_{photon} = 0}$

but $|\mathbf{k}_{\text{photon}}| \ll |\mathbf{k}_f|, |\mathbf{k}_i|$ ($\lambda_{\text{photon}} \gg \lambda_f, \lambda_i$), $\therefore$ transition forbidden unless $\mathbf{k}_f - \mathbf{k}_i \simeq 0$

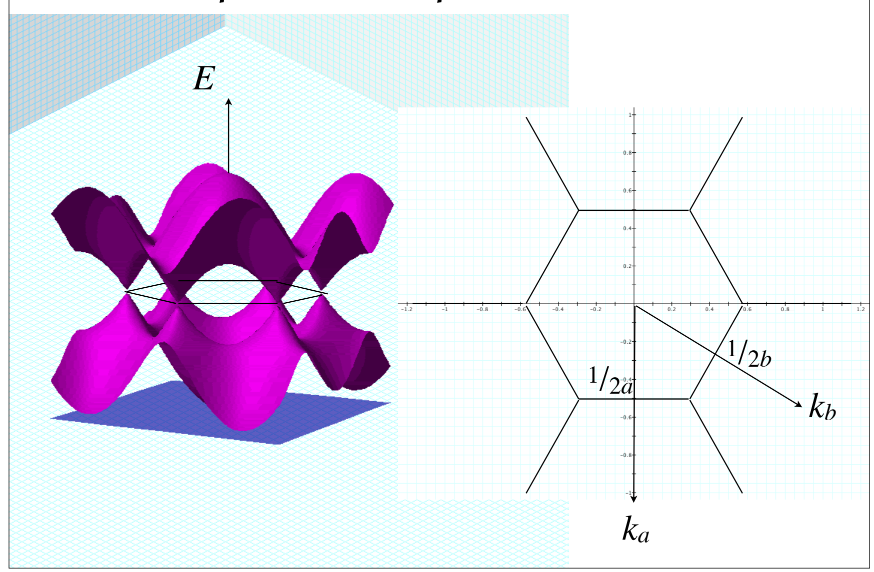
$\boxed{\text{Allowed transitions are } \textit{vertical}, \ \mathbf{k}_f \simeq \mathbf{k}_i}$

2-D Square H array - Band

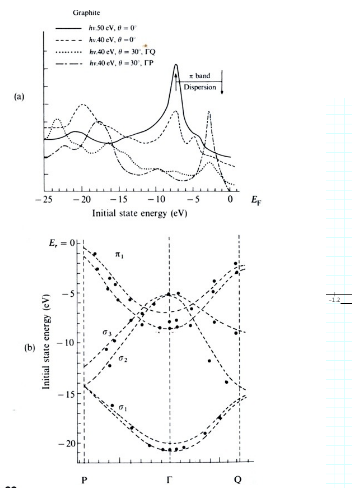



MARCH 2, 2009
C&EN
CHEMICAL & ENGINEERING NEWS
STIMULUS FUNDING
Key science agencies look to spend their share P.36
ACS IN SALT LAKE CITY
Events planned for national meeting P.57
GRAPHENE ON THE HORIZON
Thinnest carbon is thick with promise P.14
PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY

2-D Graphite (Graphene) π *Bands*



PES Measurements of Graphite



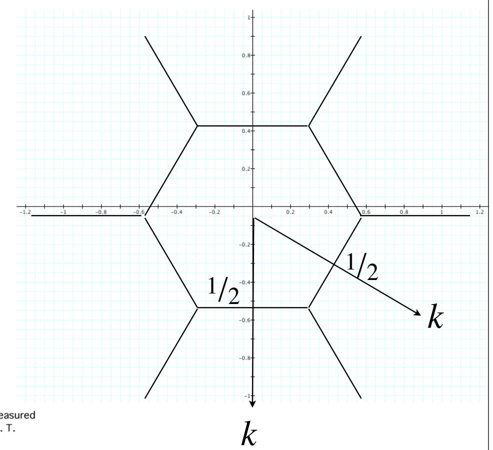


Fig. 4.29
Experimental band structure of graphite. (a) Photoelectron spectra measured at different angles. (b) $E(k)$ curves deduced from the spectra. (From L. T. McGovern *et al.*, *Physica B*, **99** (1980), 415.)

Densities of States for 1D, 2-D, 3-D