PHYSICS 220 : GROUP THEORY
FINAL EXAMINATION SOLUTIONS

This exam is due in my office, 5438 Mayer Hall, at 9 am, Monday, June 6. You are allowed to use the course lecture notes, the Lax text, and the character tables (link from lecture notes web page), but no other sources, and please do not discuss the exam with anyone other than me, other than to reassure your classmates that indeed this is a most fair and excellent exam.

[**1**] C_{20} is the smallest fullerene. It has the structure of a dodecahedron, *i.e.* a threefold coordinated cage with 20 sites arranged in 12 pentagonal faces and 30 edges. Its symmetry group is I_h.

(a) Similar story to C_{60} : The sp^2 hybridized orbitals account for three of the four electrons in the 2s and 2p shells. (The 1s shell is completely inert.) The remaining orbital is the π orbital, oriented along a line from each carbon atom to the center of the molecule. Such orbitals transform trivially under I_h. Consider a tight-binding Hamiltonian

$$\hat{H} = -t \sum_{\langle ij \rangle} \Big(|\, i \,\rangle \langle \, j \,| + |\, j \,\rangle \langle \, i \,| \Big) \quad ,$$

where $|\, i \,\rangle$ and $|\, j \,\rangle$ are π-orbitals for neighboring carbon atoms i and j. Classify the multiplets in the tight binding eigenspectrum according to IRREPs of I_h. For extra credit, write a computer program which diagonalizes $\hat{H}$ for $t = 1$ and plot the spectrum, labeling each multiplet accordingly.

Solution : We have $\chi^{\mathsf{per}}(E) = 20$, $\chi^{\mathsf{per}}(20C_3) = 2$, and $\chi^{\mathsf{per}}(15\sigma) = 4$. All other classes have $\chi^{\mathsf{per}}(\mathcal{C}) = 0$. Thus, with $N_{I_h} = 120$,

$$n_\Gamma(\Gamma^{\mathsf{per}}) = \frac{1}{6} \Big(\chi^\Gamma(E) + 2\chi^\Gamma(20C_3) + 3\chi^\Gamma(15\sigma) \Big) \quad ,$$

and using the decomposition formula we obtain

$$\boxed{\Gamma^{\mathsf{elec}} = \Gamma^{\mathsf{orb}} \times \Gamma^{\mathsf{per}} = A_g \oplus G_g \oplus H_g \oplus T_{1u} \oplus T_{2u} \oplus G_u}$$

the total dimension of which is 20.

(b) If pressure is applied to opposite pentagonal faces, the symmetry is broken from I_h down to D_{5d}. Find how the tight-binding multiplets from part (a) split into D_{5d} IRREPs.

Solution : For D_{5d}, we lose the C_3 (and S_6) operations. The order of the group is $N_{D_{5d}} = 20$, and we have the decomposition

$$n_\Gamma(\Gamma^{\mathsf{per}}) = \frac{1}{20} \Big(20\,\chi^\Gamma(E) + 4 \cdot 5\,\chi^\Gamma(5\sigma) \Big) = \chi^\Gamma(E) + \chi^\Gamma(5\sigma) \quad .$$

Decomposing in D_{5d} using the character table,

$$\boxed{\Gamma^{\mathsf{elec}} = 2A_{1g} \oplus 2E_{1g} \oplus 2E_{2g} \oplus 2A_{2u} \oplus 2E_{1u} \oplus 2E_{2u}}$$

whose total dimension is again 20. Decomposing relevant the I_h IRREPs in D_{5d}, we find

$$\begin{aligned} A_{1g} &= A_{1g} & T_{1u} &= A_{2u} \oplus E_{1u} \\ G_g &= E_{1g} \oplus E_{2g} & T_{2u} &= A_{2u} \oplus E_{2u} \\ H_g &= A_{1g} \oplus E_{1g} \oplus E_{2g} & G_u &= E_{1u} \oplus E_{2u} \quad , \end{aligned}$$

and the decompositions agree.

(c) Classify all vibrational modes of C_{20} according to IRREPs of I_h. Indicate whether each multiplet is IR active, Raman active, or Raman silent. If you really want to impress me, find the normal modes numerically for a ball and spring model, where all masses and spring constants are the same.

Solution : We first construct $\Psi = \Gamma^{\mathsf{vec}} \times \Gamma^{\mathsf{per}}$, for which $\chi^{\Psi}(E) = 3 \times 20 = 60$, $\chi^{\Psi}(15\sigma) = 1 \times 4 = 4$. The decomposition formula for Ψ is thus $n_{\Gamma}(\Psi) = \frac{1}{2}\chi^{\Gamma}(E) + \frac{1}{2}\chi^{\Gamma}(15\sigma)$. Appealing to the character table for I_h we find

$$\Psi = A_g \oplus T_{1g} \oplus T_{2g} \oplus 2G_g \oplus 3H_g \oplus 2T_{1u} \oplus 2T_{2u} \oplus 2G_u \oplus 2H_u \quad .$$

To obtain Γ^{vib}, we must subtract from Ψ the zero modes from $\Gamma^{\mathsf{vec}} = T_{1u}$ (translations) and $\Gamma^{\mathsf{rot}} = T_{1g}$ (rotations). Thus,

$$\boxed{\Gamma^{\mathsf{vib}} = \boldsymbol{A_g} \oplus \boldsymbol{T_{2g}} \oplus \boldsymbol{2G_g} \oplus \boldsymbol{3H_g} \oplus T_{1u} \oplus 2T_{2u} \oplus 2G_u \oplus 2H_u}$$

Only the T_{1u} (blue) multiplet is IR active. To check Raman activity, we need Γ^{sym} from the symmetrized product of vector representations. It is an easy matter to decompose $\Gamma^{\mathsf{vec}} \times \Gamma^{\mathsf{vec}} = A_g \oplus T_{1g} \oplus H_g$. The total dimension is nine, corresponding to a real 3×3 matrix. We only need the symmetric part, which is of dimension six, so clearly T_{1g}, which is of dimension three, corresponds to Γ^{asy} and therefore $\Gamma^{\mathsf{sym}} = A_g \oplus H_g$. The four *ungerade* multiplets are Raman inactive (blue/red), and among the *gerade* multiplets, only A_g and H_g are active (bold black); the others are silent (bold gray).

Nota bene : Sami Ortoleva astutely discovered several errors in the Atkins, Child, and Phillips character table for I_h (their I table is OK). I have corrected the error in the linked file on the Physics 220 Lecture Notes web page. Original version at

`http://www3.uji.es/~planelle/APUNTS/TGS/taules_TG_oxford.pdf`

[2] Consider the structure in Fig. 2, which is the Shastry-Sutherland lattice with nonsymmorphic wallpaper group $p4g$ (from Fig. 5.11 of the notes).

(a) Let the length of each bond be a. Choose as the origin the center of the figure, and find expressions for the four basis vectors $\boldsymbol{\delta}_{1,2,3,4}$ corresponding to the red, yellow, grey, and blue sites in the first Wigner-Seitz cell (counterclockwise starting from the right, for the color blind among you). You may assume that the smaller of the two internal angles of each rhombus is α.

Solution : We have

$$\boxed{\boldsymbol{\delta}_{1,3} = \pm a \sin(\tfrac{1}{2}\alpha)\,\hat{\boldsymbol{x}} \qquad , \qquad \boldsymbol{\delta}_{2,4} = \pm a \cos(\tfrac{1}{2}\alpha)\,\hat{\boldsymbol{y}}}$$

(b) Find two elementary direct lattice vectors $\boldsymbol{a}_{1,2}$. Find the corresponding reciprocal lattice vectors $\boldsymbol{b}_{1,2}$.

Solution : The primitive direct lattice vectors are chosen to be

$$\boxed{\boldsymbol{a}_1 = \frac{a_0}{\sqrt{2}}\,(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}) \qquad , \qquad \boldsymbol{a}_2 = \frac{a_0}{\sqrt{2}}\,(-\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}})}$$

with $a_0 = \sqrt{2}\,a\big(\cos(\tfrac{1}{2}\alpha) + \sin(\tfrac{1}{2}\alpha)\big)$. The elementary reciprocal lattice vectors are then

$$\boxed{\boldsymbol{b}_1 = \frac{\sqrt{2}\pi}{a_0}\,(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}) \qquad , \qquad \boldsymbol{b}_2 = \frac{\sqrt{2}\pi}{a_0}\,(-\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}})}$$

(c) Find the scattering form factor $F(\boldsymbol{K})$ defined in Eqn. 5.16 of the notes and show there are extinctions in the Bragg pattern.

Solution : The form factor is

$$F(\boldsymbol{K}) = \bigg|\sum_{i=1}^{4} e^{-i\boldsymbol{K}\cdot\boldsymbol{\delta}_i}\bigg|^2 \quad .$$

We write $\boldsymbol{K} = n_1\boldsymbol{b}_1 + n_2\boldsymbol{b}_2$. Now

$$\boldsymbol{b}_1\cdot\boldsymbol{\delta}_{1,3} = \pm\frac{\pi s}{s+c} \quad , \quad \boldsymbol{b}_1\cdot\boldsymbol{\delta}_{2,4} = \pm\frac{\pi c}{s+c} \quad , \quad \boldsymbol{b}_2\cdot\boldsymbol{\delta}_{1,3} = \mp\frac{\pi s}{s+c} \quad , \quad \boldsymbol{b}_2\cdot\boldsymbol{\delta}_{2,4} = \pm\frac{\pi c}{s+c} \quad .$$

It is convenient to define

$$\theta = \frac{\pi s}{s+c} \qquad , \qquad \pi - \theta = \frac{\pi c}{s+c} \quad ,$$

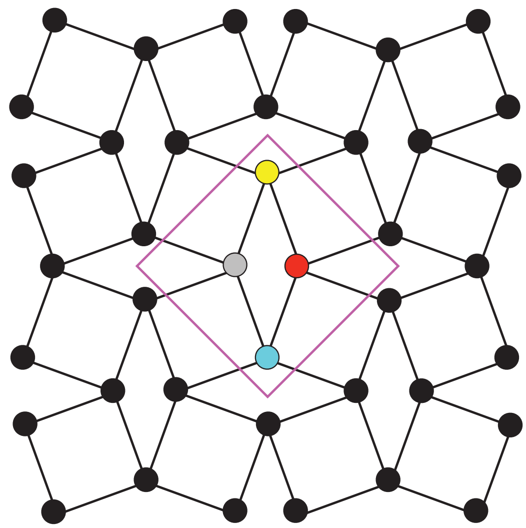

Figure 1: A lattice with $p4g$ symmetry.

where $s = \sin(\frac{1}{2}\alpha)$ and $c = \cos(\frac{1}{2}\alpha)$. Thus,

$$\boldsymbol{K} \cdot \boldsymbol{\delta}_{1,3} = \pm(n_1 - n_2)\,\theta \quad , \quad \boldsymbol{K} \cdot \boldsymbol{\delta}_{2,4} = \pm(n_1 + n_2)(\pi - \theta) \quad ,$$

and therefore

$$\boxed{F(\boldsymbol{K}) = 4\Big[\cos\big[(n_1 - n_2)\,\theta\big] + (-1)^{n_1+n_2}\cos\big[(n_1 + n_2)\,\theta\big]\Big]^2}$$

So for generic θ there will be extinctions in the Bragg pattern under two circumstances:

$$\boxed{\text{(i) } n_1 = 0 \text{ and } n_2 \text{ odd} \quad , \quad \text{(ii) } n_1 \text{ odd and } n_2 = 0}$$

This is all consistent with the discussion in §5.4.2 of the Lecture Notes. If $\boldsymbol{K}$ lies along the invariant line of a mirror m for a two-dimensional point group, then if $\boldsymbol{K} = n\boldsymbol{\beta}$, where $\boldsymbol{\beta}$ is a basis vector for the one-dimensional subset of the reciprocal lattice within that invariant line, we have extinctions whenever n is odd. In our problem, there are glide mirror lines along $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$. In the former case, $n_2 = 0$ and odd n_1 are extinguished. In the latter case, $n_1 = 0$ and odd n_2 are extinguished.

(d) When $\alpha = \frac{1}{2}\pi$, the lattice becomes square. Explain the Bragg extinctions in this case.

When $\alpha = \frac{1}{2}\pi$ we have $\theta = \frac{1}{2}\pi$ and $F(\boldsymbol{K}) = 16\cos^2(\frac{1}{2}\pi n_1)\cos^2(\frac{1}{2}\pi n_2)$. There are then extinctions whenever either n_1 or n_2 is odd, *i.e.* only the (even , even) Bragg points survive, which are one quarter of all the Bragg points. The reason is that the Shastry-Sutherland lattice (SSL) for $\alpha = \frac{1}{2}\pi$ becomes a square lattice rotated by $\frac{1}{4}\pi$, *i.e.* a Bravais lattice with a four element basis. The only Bragg peaks are those corresponding to the small square lattice, and these are the surviving ones from the SSL structure.

$$\boxed{\text{Bragg peaks with } n_1 \text{ odd or } n_2 \text{ odd extinguished due to quadrupled unit cell}}$$

(e) How do the basis points transform under the glide mirror? *I.e.* what basis color does yellow get mapped to, *etc.*? Also indicate which glide mirror you have chosen.

Solution : There is a glide mirror parallel to $\boldsymbol{a}_1$ which intersects the link between the red and blue basis elements at its midpoint. The glide operation has the effect of exchanging blue and red, and exchanging yellow and grey:

$$\boxed{\text{mirror along } \boldsymbol{a}_1 \ : \ \mathrm{B} \leftrightarrow \mathrm{R} \ , \ \mathrm{Y} \leftrightarrow \mathrm{G}}$$

If you chose the other direction for the glide, you should find

$$\boxed{\text{mirror along } \boldsymbol{a}_2 \ : \ \mathrm{Y} \leftrightarrow \mathrm{R} \ , \ \mathrm{B} \leftrightarrow \mathrm{G}}$$

[3] Consider a V^{2+} ion in a D_4 environment.

(a) The electronic configuration is [Ar] $4s^0\,3d^3$. Hund's first two rules say $S = \frac{3}{2}$ and $L = 3$ (F). What is the ground state term according to Hund's third rule?

Solution : Hund's third rule says $J = L - S$ if an incomplete shell is not more than half filled, hence the ground state term for the isolated ion is

$$\boxed{{}^{2S+1}L_J = {}^4\mathrm{F}_{3/2}}$$

(b) Using the notation of Atkins, Child, and Phillips, the double group D_4' has two spin representations, $E_{1/2}$ and $E_{3/2}$, both of which are two-dimensional. Ignoring spin-orbit, decompose F into IRREPs of D_4 (the decomposition will be the same in D_4'). You may find some of the results in Tab. 6.5 of the notes useful (*e.g.* for the characters of certain rotations in the $l = 3$ representation of $\mathsf{O}(3)$). Then decompose

D_4	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	
A_1	1	1	1	1	1	
A_2	1	1	1	-1	-1	
B_1	1	-1	1	1	-1	
B_2	1	-1	1	-1	1	
E	2	0	-2	0	0	
P	3	1	-1	-1	-1	$A_2 \oplus E$
D	5	-1	1	1	1	$A_1 \oplus B_1 \oplus B_2 \oplus E$
F	7	-1	-1	-1	-1	$A_2 \oplus B_1 \oplus B_2 \oplus 2E$

Table 1: Character table of D_4 and decomposition of $L = 1$, 2, and 3 multiplets in a D_4 environment.

the $\varGamma_{3/2}$ representation for $S = \frac{3}{2}$ in D'_4. (Hint: it can give only some combination of the two spin IRREPs.) Finally, decompose the product $\varGamma_{3/2} \times \mathrm{F} = {}^4\mathrm{F}$ and find the IRREPs for all crystal field levels. Once again, your answer can only involve the $E_{1/2}$ and $E_{3/2}$ IRREPs, so in the end this isn't so nasty. For a template of how to proceed, see the section "Co^{++} in a cubic environment" in §6.2.6 of the notes. You may find Tab. 6.10 helpful as well.

Solution : With the help of the aforementioned tables, we construct Tab. 1, which we use to decompose F into D_4 IRREPs. We also must decompose $\varGamma_{3/2}$ in terms of the spin IRREPs of D'_4, using Tab. 2. Finally, we must multiply the spinless and spin IRREPs, which we do in Tab. 3. We arrive at the result

$$\boxed{\varGamma_{3/2} \times \mathrm{F} = \Big(E_{1/2} \oplus E_{3/2}\Big) \times \Big(A_2 \oplus B_1 \oplus B_2 \oplus 2E\Big) = 7E_{1/2} \oplus 7E_{3/2}}$$

Note that the total dimension is 28, corresponding to the product of the four-dimensional $\varGamma_{3/2}$ and the seven-dimensional F $\mathsf{SO}(3)$ IRREPs.

(c) Starting on the dominant LS coupling end, decompose ${}^4\mathrm{F}$ into IRREPs of $\mathsf{O}(3)$, *i.e.* by good old addition of angular momentum. Then decompose into D'_4 IRREPs and check that you get the same answer as in part (b).

Solution : Within $\mathsf{SO}(3)$, we have

$$\boxed{\varGamma_{3/2} \times \mathrm{F} = \varGamma_{3/2} \oplus \varGamma_{5/2} \oplus \varGamma_{7/2} \oplus \varGamma_{9/2}}$$

all of which are decomposed into D'_4 IRREPs in Tab. 2. Adding up all the decompo-

D_4'	E	$\bar{E}$	$2C_4$	$2\bar{C}_4$	C_2 $\bar{C}_2$	C_2' $\bar{C}_2'$	C_2'' $\bar{C}_2''$	
$E_{1/2}$	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0	
$E_{3/2}$	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0	
$\mathit{\Gamma}_{3/2}$	4	-4	0	0	0	0	0	$E_{1/2} \oplus E_{3/2}$
$\mathit{\Gamma}_{5/2}$	6	-4	$-\sqrt{2}$	$\sqrt{2}$	0	0	0	$E_{1/2} \oplus 2E_{3/2}$
$\mathit{\Gamma}_{7/2}$	8	-8	0	0	0	0	0	$2E_{1/2} \oplus 2E_{3/2}$
$\mathit{\Gamma}_{9/2}$	10	-10	$\sqrt{2}$	$-\sqrt{2}$	0	0	0	$3E_{1/2} \oplus 2E_{3/2}$

Table 2: Spin IRREPs for D_4' and decomposition of the $S = \frac{3}{2}$ multiplet.

D_4'	A_1	A_2	B_1	B_2	E
$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{3/2}$	$E_{3/2}$	$2E_{3/2}$
$E_{3/2}$	$E_{3/2}$	$E_{3/2}$	$E_{1/2}$	$E_{1/2}$	$2E_{1/2}$

Table 3: Products of spinless and spin IRREPs within D_4'.

sitions, we obtain once again

$$\boxed{\mathit{\Gamma}_{3/2} \times \mathrm{F} = 7E_{1/2} \oplus 7E_{3/2}}$$