Solution manual - Group Theory and Quantum Mechanics - Tinkham

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Contents

Chapter 2

Problem 2.1.

(a) For the multiplication table we obtain:

	E	A	B	C	D	F	G	H
E	E	A	B	C	D	F	G	H
A	A	E	G	H	F	D	B	C
B	B	G	E	F	H	C	A	D
C	C	F	H	E	G	A	D	B
D	D	H	F	G	E	B	C	A
F	F	C	D	B	A	G	H	E
G	G	B	A	D	C	H	E	F
H	H	D	C	A	B	E	F	G

(b) There are five classes: $G_1 = E$, $G_2 = A, B$, $G_3 = C, D$, $G_4 = G$ and $G_5 = F, H$
(c) We have the following sub classes: $\{E, A\}$,$\{E, B\}$,$\{E, C\}$,$\{E, D\}$,$\{E, G\}$,$\{E, F, G, H\}$,$\{E, A, B, G\}$,$\{E, C, D, G\}$.
For the normal divisors we have: $\{E, G\}$,$\{E, A, B, G\}$,$\{E, C, D, G\}$,$\{E, F, G, H\}$
(d) We are going to find only the right cosets: –

$$\{E, G\}\{A, B\} = \{A, B\} \quad \{E, G\}\{C, D\} = \{C, D\} \quad \{E, G\}\{F, H\} = \{F, H\}$$

$$\{E, F, G, H\}\{A, B, C, D\} = \{A, B, C, D\}$$

$$\{E, A, B, G\}\{C, D, F, H\} = \{C, D, F, H\}$$

$$\{E, C, D, G\}\{A, B, F, H\} = \{A, B, F, H\}$$

(e) The multiplication table for the last three normal divisors is trivial, so we are going to write the others only in the nontrivial cases:

	{E,G}	{A,B}	{C,D}	{F,H}
{E,G}	{E,G}	{A,B}	{C,D}	{F,H}
{A,B}	{A,B}	{E,G}	{F,H}	{C,D}
{C,D}	{C,D}	{F,H}	{E,G}	{A,B}
{F,H}	{F,H}	{C,D}	{A,B}	{E,G}

For the factor groups that contain only two elements the multiplication table is trivial and thus not written.
(f) For the multiplication of groups we have:

$$G_1 \times G_1 = G_1 \quad G_1 \times G_2 = G_2 \quad G_1 \times G_3 = G_3 \quad G_1 \times G_4 = G_4 \quad G_1 \times G_5 = G_5$$

$$G_2 \times G_2 = 2G_1 + 2G_4 \quad G_2 \times G_3 = 2G_5 \quad G_2 \times G_4 = G_2 \quad G_2 \times G_5 = 2G_3$$

$$G_3 \times G_3 = 2G_1 + 2G_4 \quad G_3 \times G_4 = G_3 \quad G_3 \times G_5 = 2G_2$$

$$G_4 \times G_4 = G_1 \quad G_4 \times G_5 = G_5$$

$$G_5 \times G_5 = 2G_1 + 2G_4$$

We don't take $G_3 \times G_2$ because in **Problem 2.8.** we show that it is the same as $G_2 \times G_3$.

Problem 2.2.

Using the notation from **Problem 2.1.** the symmetry elements are E, A, B, G. Their multiplication table is as follows:

	E	A	B	G
E	E	A	B	G
A	A	E	G	B
B	B	G	E	A
G	G	B	A	E

We have four classes, which are $G_1 = E$, $G_2 = A$, $G_3 = B$ and $G_4 = G$.

Problem 2.3.

From the multiplication table we can see that:

$$\begin{aligned} BA = F, \quad AB = D &\implies AB \neq BA \\ CA = D, \quad AC = F &\implies CA \neq AC \\ CF = B, \quad FC = A &\implies CF \neq FC \end{aligned}$$

Problem 2.4.

(a) 1. The requirement that the product of every two elements is in the group is trivially satisfied.
2. The associate law follows directly from the associative property of the natural numbers.
3. Since 1 is in the set, there is an identity operator.
4. Let us choose a random element j between 1 and $(p-1)$. Let there exist two distinct numbers k_1 and k_2 between 1 and $(p-1)$ such that:

$$jk_1 = jk_2 = i$$

with respect to the group operation. This means that:

$$jk_1 - jk_2 = (i + m_1 p) - (i + m_2 p) = p\,(m_1 - m_2) = j\,(k_1 - k_2)$$

But since $k_1 \neq k_2$ then $m_1 - m_2 \neq 0$, but since p is a prime number not contained in the group there cannot be an equality since either j or $k_1 - k_2$ must be a multiple of p, which cannot be true.
Therefore the product of every j with any k is not repeated twice, or in each column and row if we are to make a multiplication table we have no multiplicity of elements. Since the number of elements in a column or row are $(p-1)$ then one of them is the element 1, thus there exists a multiplicative inverse j^-1 in the group such that $jj^{-1} = 1$.

Now we work out the multiplication table for $p = 7$:

	1	2	3	4	5	6
1	1	2	3	4	5	6
2	2	4	6	1	3	5
3	3	6	2	5	1	4
4	4	1	5	2	6	3
5	5	3	1	6	4	2
6	6	5	4	3	2	1

(b) In (a) we showed that if we have an element j if we multiply it by different elements we get different results. Thus if we multiply j by all elements $1, 2, ..., p-1$ we should still obtain all elements, i.e. $\{1 \cdot j, 2 \cdot j, ..., (p-1) \cdot j\} = \{1, 2, ...p-1\}$.
Since we have the same elements in both sets and since the group is Abelian (due to how numbers are multiplied), if we are to multiply all elements we should obtain the same result:

$$(1 \cdot j)\,(2 \cdot j) \ldots ((p-1) \cdot j) = 1 \cdot 2 \cdot \ldots \cdot (p-1)$$

Now e take all the j's out and we obtain:

$$j^{p-1}\left(1\cdot 2\cdot \ldots \cdot (p-1)\right) = 1\cdot 2\cdot \ldots \cdot (p-1)$$

Now we multiply with the inverse element of $(p-1)!$ and obtain:

$$j^{p-1} = 1$$

(c) We claculate:

$$\begin{aligned}
2^6 &= 64\,(\text{mod}7) = 7\cdot 9 + 1\,(\text{mod}7) = 1 \\
3^6 &= 729\,(\text{mod}7) = 7\cdot 104 + 1\,(\text{mod}7) = 1 \\
5^6 &= 15625\,(\text{mod}7) = 7\cdot 2232 + 1\,(\text{mod}7) = 1
\end{aligned}$$

Problem 2.5.

Problem 2.6.

A cyclic group of order 2 has elements E, A and a cyclic group of order four has elements E, B, B^2, B^3. The homomorphism between them is:

$$E \leftrightarrow E, B^2 \qquad A \leftrightarrow B, B^3$$

Problem 2.7.

First we show that if the group is Abelian then there is an isomorphism between the elements and their inverses. Let us consider two elements A and B. Their product C is given by:

$$C = AB \implies C^{-1} = B^{-1}A^{-1} = A^{-1}B^{-1}$$

But since the group is Abelian then the inverse elements commute and we thus see that there is an isomorphism:

$$C = AB \leftrightarrow C^{-1} = A^{-1}B^{-1}$$

Now let there be an isomorphism between the elements and their inverses but let the group be non-Abelian. Then due to the isomorpishm we must have:

$$C = AB \leftrightarrow C^{-1} = A^{-1}B^{-1}$$

But the inverse of C is given by:

$$C^{-1} = B^{-1}A^{-1}$$

Since the group is non-Abelian $A^{-1}B^{-1} = B^{-1}A^{-1}$ cannot be satisfied for all elements of the group. Thus we have reached a conclusion.
In this way we have shown that a group is Abelian if and only if there exists an isomorphism between the elements and their inverses.

Problem 2.8.

We choose two classes G_i and G_j and choose one element from them $g_i \in G_i$ and $g_j \in G_j$. We obtain can write their product as:

$$g_{i\times j} = g_i g_j = g_i e g_j = g_i \underbrace{R^{-1}R}_{E} g_j,$$

where e is the identity element of the group and R is any member of the group. Let us now choose R such that we have:

$$g_i R^{-1} = g_j$$

We can make such a choice due to the theorems in Chapter 2. From this we can write:

$$g_{i\times j} = \underbrace{g_i R^{-1}}_{g_j} R \underbrace{g_j}_{g_i R^{-1}} = g_j R g_i R^{-1}$$

Now Rg_iR^{-1} is another member of the class G_i, which we will denote by g_i', from which:

$$g_{i\times j} = g_j g_i' \tag{1}$$

But since the choice of g_i andg_j was random and from (1) we conclude that:

$$G_iG_j = G_jG_i$$

Chapter 3

Problem 3.1.

(a)The number of inequivalent irreducible representations is equal to the number of classes of the group. D_4 has five classes, thus there will be five irreducible representations. Let their dimensionalities be respectively a, b, c, d, e. D_4 has 8 elements, thus we want:

$$a^2 + b^2 + c^2 + d^2 + e^2 = 8$$

From this we can see that the only possible solution (because dimensions are integers) is $a = 1$, $b = 1$, $c = 1$, $d = 1$ and $e = 2$. Thus we have 4 one-dimensional and 1 two-dimensional irreducible representations of the group.

(b) One of the one dimensional irreducible representations should be the completely symmetrical representation i.e. all of the characters for this representation should be 1. Thus we have the following table:

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
Γ_1	1	1	1	1	1
Γ_2	1	-	-	-	-
Γ_3	1	-	-	-	-
Γ_4	1	-	-	-	-
Γ_5	2	-	-	-	-

Now for each row we are going to call the unknown elements as a, b, c, d. Using the orthogonality and normalization relations we obtain the following system for the nest three represention s:

$$\begin{cases} 1 + 2a + b + 2c + 2d = 0 \\ 1 + 2a^2 + b^2 + 2c^2 + 2d^2 = 8 \end{cases}$$

This system is solved very easily, especially after seeing that a,c,d have the same role and thus can be interchanged, which would generate the different irreducible representations. Thus we have $b = 1$ and $a, c, d = \pm 1$. For the fifth irreducible representation we have:

$$\begin{cases} 2 + 2a + b + 2c + 2d = 0 \\ 2 + 2a + b - 2c - 2d = 0 \\ 2 - 2a + b + 2c - 2d = 0 \\ 2 - 2a + b - 2c - 2d = 0 \\ 4 + 2a^2 + b^2 + 2c^2 + 2d^2 = 8 \end{cases}$$

This system has a unique solution. Just add the first 4 equations and we obtain:

$$\begin{cases} 8 + 4b = 0 \\ 1 + 2a^2 + b^2 + 2c^2 + 2d^2 = 8 \end{cases}$$

From which we obtain $b = -2$, $\quad a = c = d = 0$. And we have obtained the character table.

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

Problem 3.2.

Using the general orthogonality relation from the text (3.14), we have:

$$\sum_R \chi^{(i)}(R)^* \chi^{(j)}(R) = h\delta_{ij}$$

But every group has the completely symmetrical irreducible representations which we denote as $\Gamma^{(1)}$, where each character $\chi^{(1)}(R) = 1$. Thus we apply $i = 1$ we have:

$$\sum_R \chi^{(1)}(R)^* \chi^{(j)}(R) = \sum_R \chi^{(j)}(R) = h\delta_{1j} = \begin{cases} h, & j = 1 \\ 0, & j \neq 1 \end{cases}$$

Problem 3.3.

The form of the rotation matrices is very widely known, we have to take into account that here we are rotating in the clockwise sense:

$$F = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \quad G = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \quad H = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

Now multiplying the matrices we indeed have:

$$FG = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = H$$

Problem 3.4.

Similarly to **Problem 3.2.** we use an orthogonality relation, but this time the columns orthogonality one (3.17):

$$\sum_i \chi^{(i)}(R_j)^* \chi^{(i)}(R_k) = \frac{h}{N_k}\delta_{jk}$$

This time we use:

$$l_j = \chi^{(j)}(E) = \chi^{(j)}(E)^*$$

We multiply both sides by $\chi^j(R)$ and sum over j:

$$\sum_j l_j \chi^{(j)}(R) = \sum_j \chi^{(j)}(E)^* \chi^j(R) = h\delta_{ER} = \begin{cases} h, & R = E \\ 0, & R \neq E \end{cases}$$

Similar proof can be given using the properties of the regular representation. Since the regular representation has the following properties:

$$\chi^{(reg)}(R) = \begin{cases} h, & R = E \\ 0, & R \neq E \end{cases}$$

And we know that each irreducible representation is contained as much as times in the regular representation as its dimensionality $(a_j = l_j)$ then we can easily write:

$$\chi^{(reg)}(R) = \sum_j a_j \chi^{(j)}(R) = \sum_j l_j \chi^{(j)}(R) = \begin{cases} h, & R = E \\ 0, & R \neq E \end{cases}$$

Problem 3.5.

We use the right-hand rule to define a positive direction of rotation. From this we can easily obtain the rotation matrices about each of the axes. We have:

$$\hat{R}_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \quad \hat{R}_y(\theta) = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \quad \hat{R}_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Now we compute the following products:

$$\hat{R}_x(\theta_x)\hat{R}_y(\theta_y) = \begin{pmatrix}1 & 0 & 0\\ 0 & \cos\theta_x & -\sin\theta_x\\ 0 & sin\theta_x & \cos\theta_x\end{pmatrix}\begin{pmatrix}\cos\theta_y & 0 & \sin\theta_y\\ 0 & 1 & 0\\ -\sin\theta_y & 0 & \cos\theta_y\end{pmatrix} = \begin{pmatrix}\cos\theta_y & 0 & \sin\theta_y\\ \sin\theta_x\sin\theta_y & \cos\theta_x & -\sin\theta_x\cos\theta_y\\ -\sin\theta_y\cos\theta_x & \sin\theta_x & \cos\theta_x\cos\theta_y\end{pmatrix}$$

$$\hat{R}_y(\theta_y)\hat{R}_x(\theta_x) = \begin{pmatrix}\cos\theta_y & 0 & \sin\theta_y\\ 0 & 1 & 0\\ -\sin\theta_y & 0 & \cos\theta_y\end{pmatrix}\begin{pmatrix}1 & 0 & 0\\ 0 & \cos\theta_x & -\sin\theta_x\\ 0 & sin\theta_x & \cos\theta_x\end{pmatrix} = \begin{pmatrix}\cos\theta_y & \sin\theta_y\sin\theta_x & \sin\theta_y\cos\theta_x\\ 0 & \cos\theta_x & -\sin\theta_x\\ -\sin\theta_y & \cos\theta_y\sin\theta_x & \cos\theta_x\cos\theta_y\end{pmatrix}$$

From this we obtain for their commutator:

$$\left[\hat{R}_x(\theta_x), \hat{R}_y(\theta_y)\right] = \begin{pmatrix}0 & -\sin\theta_x\sin\theta_y & \sin\theta_y(1-\cos\theta_x)\\ \sin\theta_x\sin\theta_y & 0 & \sin\theta_x(1-\cos\theta_y)\\ \sin\theta_y(1-\cos\theta_x) & \sin\theta_x(1-\cos\theta_y) & 0\end{pmatrix}$$

Now for $\theta_x = \theta_y = \theta \ll 1$ we have

$$\left[\hat{R}_x(\theta), \hat{R}_y(\theta)\right] = \begin{pmatrix}0 & -\theta^2 & 0\\ \theta^2 & 0 & 0\\ 0 & 0 & 0\end{pmatrix} + o\left(\theta^2\right)$$

Now we calculate:

$$\hat{R}_z\left(\theta^2\right) - \hat{E} = \begin{pmatrix}\cos\left(\theta^2\right)-1 & -\sin\left(\theta^2\right) & 0\\ \sin\left(\theta^2\right) & \cos\left(\theta^2\right)-1 & 0\\ 0 & 0 & 1-1\end{pmatrix} = \begin{pmatrix}0 & -\theta^2 & 0\\ \theta^2 & 0 & 0\\ 0 & 0 & 0\end{pmatrix} + o\left(\theta^3\right)$$

Thus in the limit $\theta \ll 1$ the commutator and the rotation of θ^2 about Oz are equivalent.

Problem 3.6.

Let us calculate R^{-1}, S^{-1}, $(RS)^{-1} = S^{-1}R_1$, $(RS)^{-1}$:

$$R^{-1} = \begin{pmatrix}\cos\theta_y & 0 & -\sin\theta_y\\ 0 & 1 & 0\\ \sin\theta_y & 0 & \cos\theta_y\end{pmatrix} \qquad S^{-1} = \begin{pmatrix}\cos\theta_z & \sin\theta_z & 0\\ -\sin\theta_z & \cos\theta_z & 0\\ 0 & 0 & 1\end{pmatrix}$$

$$S^{-1}R^{-1} = \begin{pmatrix}\cos\theta_y\cos\theta_z & \sin\theta_z & -\cos\theta_z\sin\theta_y\\ -\cos\theta_y\sin\theta_z & \cos\theta_z & -\sin\theta_y\sin\theta_z\\ \sin\theta_y & 0 & \cos\theta_y\end{pmatrix}$$

$$R^{-1}S^{-1} = \begin{pmatrix}\cos\theta_y\cos\theta_z & \cos\theta_y\sin\theta_z & -\sin\theta_y\\ -\sin\theta_z & \cos\theta_z & 0\\ \sin\theta_y\cos\theta_z & \sin\theta_y\sin\theta_z & \cos\theta_z\end{pmatrix}$$

(a) Now we calculate the actions on the function $f = x$

$$P_R f = P_R x = x\cos\theta_y - z\sin\theta_y$$

$$P_S f = P_S x = x\cos\theta_z + y\sin\theta_z$$

$$P_S(P_R f) = P_S(P_R x) = P_S(x\cos\theta_y - z\sin\theta_y) = x\cos\theta_z\cos\theta_y + y\sin\theta_z\cos\theta_y - z\sin\theta_y$$

$$P_{SR} f = P_{SR} x = x\cos\theta_y\cos\theta_z + y\cos\theta_y\sin\theta_z - z\sin\theta_y$$

$$P_{RS} f = P_{RS} x = x\cos\theta_y\cos\theta_z + y\sin\theta_z - z\sin\theta_y\cos\theta_z$$

Suitable basis functions would be x, y, z.
(b) Now we calculate for $f = xy$:

$$P_R f = P_R xy = (x\cos\theta_y - z\sin\theta_y)\, y = xy\cos\theta_y - zy\sin\theta_y$$

$$P_S f = P_S xy = (x\cos\theta_z + y\sin\theta_z)(-x\sin\theta_z + y\cos\theta_z) = -x^2\cos\theta_z\sin\theta_z + xy\cos 2\theta_z + y^2\sin\theta_z\cos\theta_z$$

$$P_S\left(P_R f\right)=P_S\left(P_R xy\right)=P_S\left(xy\cos\theta_y-zy\sin\theta_y\right)=$$
$$=\cos\theta_y\left(-x^2\cos\theta_z\sin\theta_z+xy\cos 2\theta_z+y^2\sin\theta_z\cos\theta_z\right)-z\sin\theta_y\left(-x\sin\theta_z+y\cos\theta_z\right)=$$
$$=-x^2\cos\theta_y\cos\theta_y\sin\theta_y+xy\cos\theta_y\cos 2\theta_z+y^2\cos\theta_y\cos\theta_z\sin\theta_z+xz\sin\theta_y\sin\theta_z-zy\sin\theta_y\cos\theta_z$$
$$P_{SR}f=P_{SR}\left(xy\right)=\left(x\cos\theta_y\cos\theta_z+y\cos\theta_y\sin\theta_z-z\sin\theta_y\right)\left(-x\sin\theta_z+y\cos\theta_z\right)=$$
$$=-x^2\cos\theta_y\cos\theta_z\sin\theta_z+xy\cos\theta_y\cos 2\theta_z+y^2\cos\theta_y\cos\theta_z\sin\theta_z+xz\cos\theta_y\sin\theta_z-zy\sin\theta_y\cos\theta_z$$
$$P_{RS}f=P_{RS}xy=\left(x\cos\theta_y\cos\theta_z+y\sin\theta_z-z\cos\theta_z\sin\theta_z\right)\left(-x\cos\theta_y\sin\theta_z+y\cos\theta_z-z\sin\theta_y\sin\theta_z\right)=$$
$$=-x^2\cos^2\theta_y\sin\theta_z\cos\theta_z+y^2\cos\theta_z\sin\theta_z+z^2\sin^2\theta_y\cos\theta_z\sin\theta_z+xy\cos\theta_y\cos 2\theta_z-yz\sin\theta_y$$

Suitable basis functions would be $x^2, y^2, z^2.xy.xz, zy$.

Problem 3.7.

a) When we are searching for a basis that mean that we can write any element as a linear combination of the basis vectors. The most general way of obtaining the basis vectors is through the basis vectors generating machine, but here we will take a more intuitive approach.
Let us act with different operators on $F=x^2zg\left(r\right)$, where we will omit writing $g\left(r\right)$ as it is always invariant under point group actions. Now for D_3:

$$E\left(x^2z\right)=x^2z,\qquad C_3\left(xyz\right)=-x^2z,$$
$$C_2\left(x^2z\right)=-\frac{1}{4}x^2z-\frac{\sqrt{3}}{2}xyz-\frac{1}{4}y^2z$$
$$C_1\left(x^2z\right)=-\frac{1}{4}x^2z+\frac{\sqrt{3}}{2}xyz-\frac{3}{4}y^2z$$
$$C_{120}\left(x^2z\right)=\left(-\frac{1}{2}x+\frac{\sqrt{3}}{2}y\right)^2z=\frac{1}{4}x^2z-\frac{\sqrt{3}}{2}xyz+\frac{3}{4}y^2z,$$
$$C_{240}\left(x^2z\right)=\left(-\frac{1}{2}x-\frac{\sqrt{3}}{2}y\right)^2z=\frac{1}{4}x^2z+\frac{\sqrt{3}}{2}xyz+\frac{3}{4}y^2z$$

From this we can clearly see that the basis vectors are: $\{x^2z, xyz, y^2z\}$
b) We must find the character of the operators. We can check what are the diagonal elements for only of the group action belonging to different classes. We can thus easily write:

$$\Gamma\left(E\right)=\begin{pmatrix}1&&\\&1&\\&&1\end{pmatrix},\qquad\Gamma\left(C_3\right)=\begin{pmatrix}-1&&\\&-1&\\&&1\end{pmatrix},\qquad\Gamma\left(C_{120}\right)\begin{pmatrix}\frac{1}{4}&&\\&-\frac{1}{2}&\\&&\frac{1}{4}\end{pmatrix}$$

Thus by writing the character table we can decompose this representation into irreducible ones:

D_4	E	$2C_3$	$3C_2$	$\sum_i a_i\Gamma^{(i)}$
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	
Γ	3	-1	0	A_2+E

c) Through some calculations or through intuition we can say that the following set is orthonormal:

$$\{\frac{1}{2}z\left(x^2-y^2\right),\frac{1}{2}z\left(x^2+y^2\right),xyz\}$$

d) For this part we must use the projection operators:

$$P^{(A_2)}\left(x^2z\right)=\frac{1}{6}\left(x^2z+\frac{x^2z}{4}-\frac{\sqrt{3}}{2}xyz+\frac{3}{4}y^2z+\frac{x^2z}{4}+\frac{\sqrt{3}}{2}xyz+\frac{3}{4}y^2z+x^2z+\frac{x^2z}{4}+\frac{zy^2}{4}+\frac{zx^2}{4}+\frac{zy^2}{4}\right)$$
$$=\frac{1}{2}z\left(x^2-y^2\right)$$

$$P^{(E)}\left(x^2 z\right)=\frac{2}{6}\left(2x^2 z-\left(\frac{x^2 z}{2}+\frac{3}{2}zy^2\right)\right)=\frac{1}{2}z\left(x^2-y^2\right)$$

Thus we can finally write:

$$x^2 z=\frac{1}{2}z\left(x^2-y^2\right)+\frac{1}{2}z\left(x^2+z^2\right)$$

Problem 3.8.

The character table for D_4 is:

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

The character table for the i group (actually it is S_2) is:

i	E	i
A_g	1	1
A_u	1	-1

Now taking the direct product we obtain D_{4h}:

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	σ_{2v}	σ_{2d}
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	+1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0

Problem 3.9.

a)We choose the notation A,B,C,D as was already used in the problems of chapter 2. For each of the irreducible representations we have:

A_1:

$$\Gamma^{(A_1)}(E)=(1)\qquad \Gamma^{(A_1)}(C_4)=(1)$$
$$\Gamma^{(A_1)}\left(C_4^2\right)=(1)\qquad \Gamma^{(A_1)}\left(C_4^3\right)=(1)$$
$$\Gamma^{(A_1)}(A)=(1)\qquad \Gamma^{(A_1)}(B)=(1)$$
$$\Gamma^{(A_1)}(C)=(1)\qquad \Gamma^{(A_1)}(D)=(1)$$

A_2 :

$$\Gamma^{(A_2)}(E)=(1)\qquad \Gamma^{(A_2)}(C_4)=(1)$$
$$\Gamma^{(A_2)}\left(C_4^2\right)=(1)\qquad \Gamma^{(A_1)}\left(C_4^3\right)=(1)$$

$$\Gamma^{(A_1)}(A) = (1) \qquad \Gamma^{(A_1)}(B) = (1)$$
$$\Gamma^{(A_1)}(C) = (1) \qquad \Gamma^{(A_1)}(D) = (1)$$

B_1 :

Problem 3.10.

For the D_3 group we have:

$D_3 \times D_3$	E	$2C_3$	$3C_2$	$\sum_i a_i \Gamma^{(i)}$
$A_1 \times A_1$	1	1	1	A_1
$A_1 \times A_2$	1	1	-1	A_2
$A_1 \times E_1$	2	-1	0	E_1
$A_2 \times A_2$	1	1	1	A_1
$A_2 \times E_1$	2	-1	0	E_1
$E_1 \times E_1$	4	1	0	$A_1 + A_2 + E_1$

Problem 3.11.

For D_4 we have

$D_4 \times D_4$	E	C_2	$2C_4$	$2C_2'$	$2C_2''$	$\sum_i a_i \Gamma^{(i)}$
$A_1 \times A_1$	1	1	1	1	1	A_1
$A_1 \times A_2$	1	1	1	-1	-1	A_2
$A_1 \times B_1$	1	1	-1	1	-1	B_1
$A_1 \times B_2$	1	1	-1	-1	1	B_2
$A_1 \times E_1$	2	-2	0	0	0	E_1
$A_2 \times A_2$	1	1	1	1	1	A_2
$A_2 \times B_1$	1	1	-1	-1	1	B_2
$A_2 \times B_2$	1	1	-1	1	-1	B_1
$A_2 \times E_1$	2	-2	0	0	0	E
$B_1 \times B_1$	1	1	1	1	1	A_1
$B_1 \times B_2$	1	1	1	-1	-1	A_2
$B_1 \times E_1$	2	-2	0	0	0	E
$B_2 \times B_2$	1	1	1	1	1	A_1
$B_2 \times E_1$	2	-2	0	0	0	E_1
$E_1 \times E_1$	4	4	0	0	0	$A_1 + A_2 + B_1 + B_2$

For O we have:

$D_4 \times D_4$	E	$8C_3$	$3C_2$	$6C_2'$	$6C_4$	$\sum_i a_i \Gamma^{(i)}$
$A_1 \times A_1$	1	1	1	1	1	A_1
$A_1 \times A_2$	1	1	1	-1	-1	A_2
$A_1 \times E_1$	2	-1	2	0	0	E_1
$A_1 \times T_1$	3	0	-1	-1	1	T_1
$A_1 \times T_2$	3	0	-1	1	-1	T_2
$A_2 \times A_2$	1	1	1	1	1	A_1
$A_2 \times E_1$	2	-1	2	0	0	E_1
$A_2 \times T_1$	3	0	-1	1	-1	T_2
$A_2 \times T_2$	3	0	-1	-1	1	T_1
$E_1 \times E_1$	4	1	4	0	0	$A_1 + A_2 + E$
$E_1 \times T_1$	6	0	-2	0	0	$T_1 + T_2$
$E_1 \times T_2$	6	0	-2	0	0	$T_1 + T_2$
$T_1 \times T_1$	9	0	1	1	1	$A_1 + E_1 + T_1 + T_2$
$T_1 \times T_2$	9	0	1	-1	-1	$A_2 + E_1 + T_1 + T_2$
$T_2 \times T_2$	9	0	1	1	1	$A_1 + E_1 + T_1 + T_2$

Chapter 4

Problem 4.1.

Let's look at what happens when acting on $xyzf(r)$ when acting with a single operator from each of the classes: E, C_3 we are going to choose the triangle in the all-positive octant, for axis of C_2 and C_4 we choose Oz, and for C_2' we choose the axis passing in the middle of the line connecting the positive x and y coordinates. From this we can see that:

$$E(xyz) = xyz, \quad C_3(xyz) = xyz, \quad C_2(xyz) = (-x)(-y)z = xyz$$

$$C_4(xyz) = y(-x)z = -xyz, \quad C_2'(xyz) = -xyz$$

Thus we can see that xyz has no partners and for brevity we have removed $f(r)$. Now we can see that we have the followig characters:

$$\chi(E) = 1, \quad \chi(C_3) = 1, \quad \chi(C_2) = 1, \quad \chi(C_4) = -1, \quad \chi\left(C_2'\right) = -1$$

Thus we can say that $xyzf(r)$ belongs to the irreducible representation A_2.

Note: The most rigorous way of showing this is through the projection operators, but when I can skip this procedure, I will.

Problem 4.2.

Problem 4.3.

We have to split each irreducible representation of O under the group D_4. For this we construct the following table:

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	
O	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	$\sum_i a_i$
A_1	1	1	1	1	1	A_1
A_2	1	1	-1	-1	1	B_2
E	2	2	0	0	2	$B_1 + A_1$
T_1	3	-1	1	-1	-1	$A_2 + E$
T_2	3	-1	-1	-1	1	$B_2 + E$

Since we now have how each term splits, we can write the splitting from D_4:

$$D_0 = A_1$$

$$D_1 = T_1 = A_2 + E$$

$$D_2 = E + T_2 = A_1 + B_1 + B_2 + E$$

$$D_3 = A_2 + T_1 + T_2 = A_2 + 2B_2 + 2E$$

From this we have obtained only the symmetries. To know what are the energy levels more detailed calculations should be made as in LFT (Ligand Field Theory).

Problem 4.4.

The tetragonal double group has two additional irreducible representations Γ_6 and Γ_7. The characters of the double group are calculated using the rules provided in the text. Also the characters of the atom with spin $\frac{3}{2}$ is calculated through the formula in the text:

$$\chi_J(\alpha) = \frac{\sin\left(J+\frac{1}{2}\right)\alpha}{\sin\frac{\alpha}{2}}$$

From which we obtain the following table:

RD_4	E	R	C_2+RC_2	$2C_4$	$2RC_4$	$2C_2'+2RC_2'$	$2C_2''+2RC_2''$
Γ_1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	-1	-1
Γ_3	1	1	1	-1	-1	1	-1
Γ_4	1	1	1	-1	-1	-1	1
Γ_5	2	2	-2	0	0	0	0
Γ_6	2	-2	0	$\sqrt{2}$	$-\sqrt{2}$	0	0
Γ_7	2	-2	0	$\sqrt{2}$	$-\sqrt{2}$	0	0
$D_{\frac{3}{2}}$	4	-4	0	0	0	0	0

From this we can see the that the quadruplet $D_{\frac{3}{2}}$ splits into two doublets:

$$D_{\frac{3}{2}} \to \Gamma_6 + \Gamma_7$$

Problem 4.5.

Problem 4.6.

To solve this problem we use the projecting operators and a little trick. First let's see if H' belongs to A_1.

$$\begin{aligned}
24P^{(A_1)}\left(H'\right) = & \underbrace{\left(Ax^2+By^2-(A+B)z^2\right)}_{E} + \underbrace{\left(3Ax^2+3By^2-3(A+B)z^2\right)}_{3C_2} \\
& + \underbrace{\left(-4(A+B)x^2-4(A+B)y^2+4Bx^2+4Ay^2+4Bz^2+4Az^2\right)}_{8C_3} + \\
& + \underbrace{\left(2Ay^2+2Bx^2-2(A+B)z^2+2Az^2+2By^2-2(A+B)x^2+2Ax^2+2Bz^2-2(A+B)y^2\right)}_{6C_2} \\
& + \underbrace{\left(2Ay^2+2Bx^2-2(A+B)z^2+2Ax^2+2Bz^2-2(A+B)y^2+2Az^2+2By^2\right)}_{C_4} = \\
& = 0
\end{aligned}$$

Thus it does not belong to the A_1 representation. More importantly we can see that the last two brackets are zero, and it doesn't matter what the coefficient of the character is infort. From this we can guess that H' belongs the E irreducible representation, because there the characters of the corresponding transforamtions are 0.
But we will carry out the calculations anyway:

$$\begin{aligned}
12P^{(E)}\left(H'\right) &= 2\left(Ax^2+By^2-(A+B)z^2\right) + 2\left(3Ax^2+3By^2-3(A+B)z^2\right) \\
&- \left(-4(A+B)x^2-4(A+B)y^2+4Bx^2+4Ay^2+4Bz^2+4Az^2\right) = \\
&= 12Ax^2+12By^2-12(A+B)z^2
\end{aligned}$$

$$\implies P^{(E)}\left(H'\right) = H'$$

Thus we have confirmed our guess.

Problem 4.7.

We can solve this problem more easily starting backwards. We will find the partners of $z\left(x^2-y^2\right)$ first. From the form we can easily guess that its partners must also have the form of a variable x or y multiplied by the difference of the square of the other two. We can obtain this form by applying group operations. As the result should be a linear combination of the elements in the irreducible representation.

Thus we try first rotating by 90° about the x-axis and then about the y-axis.

$$\Gamma\left(C_{4x}\right)\left(z\left(x^2-y^2\right)\right)=-y\left(x^2-z^2\right)=y\left(z^2-x^2\right)$$

$$\Gamma\left(C_{4y}\right)=x\left(z^2-y^2\right)$$

Whichever way of writing them we choose, doesn't matter because it changes the result only up to ±1. Now we apply group operations to all of them:

$$\Gamma(E)\begin{pmatrix} z\left(x^2-y^2\right) \\ y\left(z^2-x^2\right) \\ x\left(z^2-y^2\right)\end{pmatrix}=\begin{pmatrix} z\left(x^2-y^2\right) \\ y\left(z^2-x^2\right) \\ x\left(z^2-y^2\right)\end{pmatrix} \qquad \Gamma(i)\begin{pmatrix} z\left(x^2-y^2\right) \\ y\left(z^2-x^2\right) \\ x\left(z^2-y^2\right)\end{pmatrix}=\begin{pmatrix} -z\left(x^2-y^2\right) \\ -y\left(z^2-x^2\right) \\ -x\left(z^2-y^2\right)\end{pmatrix}$$

$$\Gamma\left(C_2\right)\begin{pmatrix} z\left(x^2-y^2\right) \\ y\left(z^2-x^2\right) \\ x\left(z^2-y^2\right)\end{pmatrix}=\begin{pmatrix} z\left(x^2-y^2\right) \\ -y\left(z^2-x^2\right) \\ -x\left(z^2-y^2\right)\end{pmatrix} \qquad \Gamma\left(C_2'\right)\begin{pmatrix} z\left(x^2-y^2\right) \\ y\left(z^2-x^2\right) \\ x\left(z^2-y^2\right)\end{pmatrix}=\begin{pmatrix} -z\left(x^2-y^2\right) \\ x\left(z^2-y^2\right) \\ y\left(z^2-x^2\right)\end{pmatrix}$$

$$\Gamma\left(C_4\right)\begin{pmatrix} z\left(x^2-y^2\right) \\ y\left(z^2-x^2\right) \\ x\left(z^2-y^2\right)\end{pmatrix}=\begin{pmatrix} -z\left(x^2-y^2\right) \\ -x\left(z^2-y^2\right) \\ y\left(z^2-x^2\right)\end{pmatrix}$$

From this we have the following five characters:

$$\chi(E)=3, \quad \chi(i)=-3, \quad \chi\left(C_2\right)=-1, \quad \chi\left(C_2'\right)=1, \quad \chi\left(C_4\right)=-1$$

Which immediately tells us that the irreducible representation to which the three functions belong is T_2u. That is to show us also that we need't find all characters as well.

Problem 4.8.

Chapter 5

Problem 5.1.

From $\hat{J} = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$, we have:

$$P_\theta \psi(\varphi) = e^{-\frac{i}{\hbar}\theta\hat{J}}\psi(\varphi) = \sum_{k=0}^{\infty}\frac{1}{k!}\left(-\frac{i}{\hbar}\theta\hat{J}\right)^k \psi(\varphi) = \sum_{k=0}^{\infty}\frac{(-\theta)^k}{k!}\frac{\partial^k\psi}{\partial\varphi^k} = \sum_{k=0}^{\infty}\frac{((\varphi-\theta)-\varphi)^k}{k!}\frac{\partial^k\psi}{\partial\varphi^k} \equiv \psi(\varphi-\theta)$$

Problem 5.2.

From equation (5-35) in the book we have:

$$D^{(j)}_{m'm}(\alpha,\beta,\gamma) = e^{-i(m'\alpha+m\gamma)}\sum_k \frac{(-1)^k\sqrt{(j+m)!\,(j-m)!\,(j+m')!\,(j-m')!}}{k!\,(j+m-k)!\,(j-m'-k)!\,(k+m'-m)!}\underbrace{\left(\cos\frac{\beta}{2}\right)^{2j-2k-m'+m}\left(\sin\frac{\beta}{2}\right)^{2k+m'-m}}_{a_k}$$

Now we let $m=j$ and we obtain:

$$D^{(j)}_{m'j}(\alpha,\beta,\gamma) = e^{-i(m'\alpha+j\gamma)}\sum_k \frac{(-1)^k\sqrt{(j+j)!\,(j-j)!\,(j+m')!\,(j-m')!}}{k!\,(j+j-k)!\,(j-m'-k)!\,(k+m'-j)!}a_k =$$
$$= e^{-i(m'\alpha+m\gamma)}\sum_k \frac{(-1)^k\sqrt{(2j)!\,(j+m')!\,(j-m')!}}{k!\,(2j-k)!\,((j-m')-k)!\,(k-(j-m'))!}a_k$$

From the denominator we see that $(j-m')-k>0 \implies k-(j-m')<0$. Whenever this is the case the denominator becomes infinite (due to the properties of the $\Gamma(z)$) and the term becomes zero. Only when $(j-m')-k=0$ do we not get infinities. Thus the sum reduces to:

$$D^{(j)}_{m'j} = (-1)^{j-m'}e^{-i(m'\alpha+j\gamma)}\sqrt{\frac{(2j)!}{(j-m')!\,(j+m')!}}\left(\cos\frac{\beta}{2}\right)^{j+m'}\left(\sin\frac{\beta}{2}\right)^{j-m'}$$

Problem 5.3.

(a) The probability for a particle with arbitrary j is:

$$p_{m\to m'} = \left|\hat{D}^{(j)}(0,\theta,0)\right|^2 = \left|\sum_k \frac{(-1)^k\sqrt{(j+m)!\,(j-m)!\,(j+m')!\,(j-m')!}}{k!\,(j+m-k)!\,(j-m'-k)!\,(k+m'-m)!}\left(\cos\frac{\beta}{2}\right)^{2j-2k-m'+m}\left(-\sin\frac{\beta}{2}\right)^{2k+m'-m}\right|$$

(b) We can write the answers in terms of matrices where on each row represents a value of m and each column represents m'. The maximum value is on the top (left) and m (m') decreases as we go down (right). Thus we have:

$$T^{(0)} = 1$$

$$T^{(\frac{1}{2})}_{m\to m'} = \begin{pmatrix} \left(\cos\frac{\theta}{2}\right)^2 & \left(\sin\frac{\theta}{2}\right)^2 \\ \left(\sin\frac{\theta}{2}\right)^2 & \left(\cos\frac{\theta}{2}\right)^2 \end{pmatrix} \tag{2}$$

$$T^{(1)}_{m\to m'} = \begin{pmatrix} \left(\frac{1+\cos\theta}{2}\right)^2 & \frac{(\sin\theta)^2}{2} & \left(\frac{1-\cos\theta}{2}\right)^2 \\ \frac{(\sin\theta)^2}{2} & (\cos\theta)^2 & \frac{(\sin\theta)^2}{2} \\ \left(\frac{1-\cos\theta}{2}\right)^2 & \frac{(\sin\theta)^2}{2} & \left(\frac{1+\cos\theta}{2}\right)^2 \end{pmatrix} \tag{3}$$

(c) Now when we specialize our results for $\theta = \frac{\pi}{2}$ we obtain:

$$T^{(0)} = 1$$

$$T^{(\frac{1}{2})}_{m\to m'} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} \tag{4}$$

$$T^{(1)}_{m\to m'} = \begin{pmatrix} \frac{1}{4} & \frac{1}{2} & \frac{1}{4} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{4} & \frac{1}{2} & \frac{1}{4} \end{pmatrix} \tag{5}$$

Problem 5.4.

The general representation of the rotational group for $j = \frac{1}{2}$ is:

$$\hat{D}^{\left(\frac{1}{2}\right)}(\alpha,\beta,\gamma) = \begin{pmatrix} e^{-i\frac{\alpha+\gamma}{2}}\cos\frac{\beta}{2} & -e^{-i\frac{\alpha-\gamma}{2}}\sin\frac{\beta}{2} \\ e^{i\frac{\alpha-\gamma}{2}}\sin\frac{\beta}{2} & e^{i\frac{\alpha+\gamma}{2}}\cos\frac{\beta}{2} \end{pmatrix} \tag{6}$$

If we think about the Eulerean rotations in order we can see that we can rotate rotate a vector pointing along the z-axis to polar coordinates (θ,φ) as:

$$\hat{D}^{\left(\frac{1}{2}\right)}(\alpha=\varphi,\beta=\theta,0) = \begin{pmatrix} e^{-i\frac{\varphi}{2}}\cos\frac{\theta}{2} & -e^{-i\frac{\varphi}{2}}\sin\frac{\theta}{2} \\ e^{i\frac{\varphi}{2}}\sin\frac{\beta}{2} & e^{i\frac{\varphi}{2}}\cos\frac{\beta}{2} \end{pmatrix} \tag{7}$$

So now when we apply our transformation to a spinor 'pointing' along Oz:

$$\hat{D}^{\left(\frac{1}{2}\right)}(\varphi,\theta,0)\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix} e^{-i\frac{\varphi}{2}}\cos\frac{\theta}{2} \\ e^{i\frac{\varphi}{2}}\sin\frac{\theta}{2} \end{pmatrix} \tag{8}$$

Now we can easily specify where is a spinor pointing to. We have to consider that two quantum states are similar up to a phase, so we have:

$$\begin{pmatrix}a_+\\a_-\end{pmatrix} = e^{i\delta}\begin{pmatrix} e^{-i\frac{\varpi}{2}}\cos\frac{\theta}{2} \\ e^{i\frac{\varphi}{2}}\sin\frac{\theta}{2} \end{pmatrix} \tag{9}$$

There also exist a phases ψ and ϕ such that we can write:

$$\begin{pmatrix}a_+\\a_-\end{pmatrix} = e^{i\psi}\begin{pmatrix} e^{-i\frac{\phi}{2}}a'_+ \\ e^{i\frac{\phi}{2}}a'_- \end{pmatrix} = e^{i\delta}\begin{pmatrix} e^{-i\frac{\varpi}{2}}\cos\frac{\theta}{2} \\ e^{i\frac{\varphi}{2}}\sin\frac{\theta}{2} \end{pmatrix} \tag{10}$$

We can easily express the angle θ and φ as:

$$\begin{cases} \cos\theta = \left|a'_+\right|^2 - \left|a'_-\right|^2 = |a_+|^2 - |a_-|^2 \\ \sin\theta = 2a'_-a'_+ = 2e^{2i\delta}a_+a_- \\ \varphi = \arg\frac{a_-}{a_+} \end{cases} \tag{11}$$

Problem 5.5.

Rotating a spinor along the y-axis can be achieved through having $\alpha = \gamma = 0$ and $\beta \neq 0$ when thinking in terms of 3-D rotation using Euler rotation matrices, and we thus have:

$$\hat{D}_y^{\left(\frac{1}{2}\right)}(\theta) \equiv \hat{D}^{\left(\frac{1}{2}\right)}(0,\theta,0) = \begin{pmatrix} \cos\frac{\theta}{2} & -\sin\frac{\theta}{2} \\ \sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{pmatrix} \tag{12}$$

For rotation along Oz, we have:

$$\hat{D}_z^{\left(\frac{1}{2}\right)}(\theta) \equiv \hat{D}^{\left(\frac{1}{2}\right)}(0,0,\theta) = \begin{pmatrix} e^{-i\frac{\theta}{2}} & 0 \\ 0 & e^{i\frac{\theta}{2}} \end{pmatrix} \tag{13}$$

If we want to carry out a rotation about Ox using Euler angles we must first rotate the y-axis to take the place of Ox, then rotate about Oy the angle θ we want, and finally rotate such that Ox return to it's place. Which translated to our problem yields:

$$\hat{D}_x^{\left(\frac{1}{2}\right)}(\theta) \equiv \hat{D}^{\left(\frac{1}{2}\right)}\left(-\frac{\pi}{2},-\theta,\frac{\pi}{2}\right) = \begin{pmatrix} \cos\frac{\theta}{2} & i\sin\frac{\theta}{2} \\ i\sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{pmatrix} \tag{14}$$

Now let us rotate a spinor 'pointing' up about x and y by π:

$$\hat{D}_y^{\left(\frac{1}{2}\right)}(\pi)\,\hat{D}_x^{\left(\frac{1}{2}\right)}(\pi)\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0 & -1\\1 & 0\end{pmatrix}\begin{pmatrix}0 & i\\i & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = -i\begin{pmatrix}1\\0\end{pmatrix}$$

Thus the phase indeed changes. Now for the case of spin-1 particle with $m = 0$ we have:

$$\hat{D}_y^{(1)}(\pi)\,\hat{D}_x^{(1)}(\pi)\begin{pmatrix}0\\1\\0\end{pmatrix} = \begin{pmatrix}0 & 0 & 1\\0 & -1 & 0\\1 & 0 & 0\end{pmatrix}\begin{pmatrix}0 & 0 & -1\\0 & -1 & 0\\-1 & 0 & 0\end{pmatrix}\begin{pmatrix}0\\1\\0\end{pmatrix} = \begin{pmatrix}0\\1\\0\end{pmatrix}$$

This shows that for spin-1 particles there is no phase difference.

Problem 5.6.

There are many tables for Clebsch-Gordan coefficients that can be used one of the most used is the one of Particle Data Group one, but for this problem even the one in Wikipedia suffices. We can immedeatly write:

$$|J=0, M=0, L=2, S=2\rangle = \frac{1}{\sqrt{5}} \underbrace{|2,2\rangle}_{|L,m_l\rangle} \underbrace{|2,-2\rangle}_{|S,m_s\rangle} - \frac{1}{\sqrt{5}} |2,1\rangle |2,-1\rangle + \frac{1}{\sqrt{5}} |2,0\rangle |2,0\rangle - \frac{1}{\sqrt{5}} |2,-1\rangle |2,1\rangle + \frac{1}{\sqrt{5}} |2,-2\rangle |2,2\rangle$$

The tensor product sign has been dropped out. From the wavefunction we can see that the probability of having $S_z = 2$ is just:

$$|\langle 2,-2| \langle 2,2|0,0,2,2\rangle|^2 = \frac{1}{5}$$

Problem 5.7.

They have made a mistake when formulating this problem.

Problem 5.8.

We will calculate the g-factor for $j = l + \frac{1}{2}$. First we have:

$$\begin{aligned} |j,m\rangle &= \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}} \left|l, m-\frac{1}{2}\right\rangle \left|\frac{1}{2}, \frac{1}{2}\right\rangle + \sqrt{\frac{l-m+\frac{1}{2}}{2l+1}} \left|l, m+\frac{1}{2}\right\rangle \left|\frac{1}{2}, -\frac{1}{2}\right\rangle \\ &= \sqrt{\frac{j+m}{2j}} \left|l, m-\frac{1}{2}\right\rangle \left|\frac{1}{2}, \frac{1}{2}\right\rangle + \sqrt{\frac{j-m}{2j}} \left|l, m+\frac{1}{2}\right\rangle \left|\frac{1}{2}, -\frac{1}{2}\right\rangle \end{aligned}$$

From this we obtain:

$$\langle j,m| S_z |j,m\rangle = \frac{j+m}{2j}\frac{1}{2} + \frac{j-m}{2j}\left(-\frac{1}{2}\right) = \frac{m+m}{4j} = \frac{m}{2j}$$

Thus the g-factor is:

$$g = 1 + \frac{\langle j,m| S_z |j,m\rangle}{m} = 1 + \frac{1}{2j} = \frac{2j+1}{2j}$$

Using the formula from the vector model (where we use $l = j - \frac{1}{2}$) we have:

$$\begin{aligned} g &= 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} = 1 + \frac{j(j+1) + \frac{3}{4} - \left(j - \frac{1}{2}\right)\left(j + \frac{1}{2}\right)}{2j(j+1)} = \\ &= 1 + \frac{j^2 + j + \frac{3}{4} - j^2 + \frac{1}{4}}{2j(j+1)} = 1 + \frac{j+1}{2j(j+1)} = 1 + \frac{1}{2j} = \frac{2j+1}{2j} \end{aligned}$$

We can see that the two result agree. The derivation for the case $j = l - \frac{1}{2}$ is the same but we obtain:

$$g = 1 - \frac{1}{2j} = \frac{2j-1}{2j}$$

Problem 5.9.

We won't calculate the relative intensities, but directly the energy differences. The following σ transitions are possible from ${}^2P_{\frac{3}{2}}$ to ${}^2S_{\frac{1}{2}}$:

$$\begin{aligned} \left|{}^2P_{\frac{3}{2}}, \frac{3}{2}\right\rangle &\to \left|{}^2S_{\frac{1}{2}}, \frac{1}{2}\right\rangle \\ \left|{}^2P_{\frac{3}{2}}, \frac{1}{2}\right\rangle &\to \left|{}^2S_{\frac{1}{2}}, -\frac{1}{2}\right\rangle \\ \left|{}^2P_{\frac{3}{2}}, -\frac{1}{2}\right\rangle &\to \left|{}^2S_{\frac{1}{2}}, \frac{1}{2}\right\rangle \\ \left|{}^2P_{\frac{3}{2}}, -\frac{3}{2}\right\rangle &\to \left|{}^2S_{\frac{1}{2}}, -\frac{1}{2}\right\rangle \end{aligned}$$

And these are the following π transitions:

$$\left|{}^2P_{\frac{3}{2}}, \frac{1}{2}\right\rangle \;\;\to \left|{}^2S_{\frac{1}{2}}, \frac{1}{2}\right\rangle$$
$$\left|{}^2P_{\frac{3}{2}}, -\frac{1}{2}\right\rangle \to \left|{}^2S_{\frac{1}{2}}, -\frac{1}{2}\right\rangle$$

Using the formulas from the previous problem we have the following g-factors:

$$g_p \equiv g_{{}^2P_{\frac{3}{2}}} = \frac{4}{3}$$
$$g_s \equiv g_{{}^2S_{\frac{1}{2}}} = 2$$

From this we calculate the energy shifts:

$$E_{{}^2P_{\frac{3}{2}},\frac{3}{2}} = \mu_B B g_p m_{{}^2P_{\frac{3}{2}},\frac{3}{2}} = \mu_B B \frac{4}{3}\frac{3}{2} = 2\mu_B B$$
$$E_{{}^2P_{\frac{3}{2}},\frac{1}{2}} = \mu_B B g_p m_{{}^2P_{\frac{3}{2}},\frac{1}{2}} = \mu_B B \frac{4}{3}\frac{1}{2} = \frac{2}{3}\mu_B B$$
$$E_{{}^2P_{\frac{3}{2}},-\frac{1}{2}} = \mu_B B g_p m_{{}^2P_{\frac{3}{2}},-\frac{1}{2}} = -\mu_B B \frac{4}{3}\frac{1}{2} = -\frac{2}{3}\mu_B B$$
$$E_{{}^2P_{\frac{3}{2}},-\frac{3}{2}} = \mu_B B g_p m_{{}^2P_{\frac{3}{2}},-\frac{3}{2}} = -\mu_B B \frac{4}{3}\frac{3}{2} = -2\mu_B B$$
$$E_{{}^2S_{\frac{1}{2}},\frac{1}{2}} = \mu_B B g_s m_{{}^2S_{\frac{1}{2}},\frac{1}{2}} = \mu_B B 2\frac{1}{2} = \mu_B B$$
$$E_{{}^2S_{\frac{1}{2}},-\frac{1}{2}} = \mu_B B g_s m_{{}^2S_{\frac{1}{2}},-\frac{1}{2}} = -\mu_B B 2\frac{1}{2} = -\mu_B B$$

Thus we have the following energy differences for the transitions:

$$\begin{cases} E_{\frac{3}{2}\to\frac{1}{2}} = \mu_B B \\ E_{\frac{1}{2}\to-\frac{1}{2}} = \frac{5}{3}\mu_B B \\ E_{-\frac{1}{2}\to\frac{1}{2}} = -\frac{5}{3}\mu_B B \\ E_{-\frac{3}{2}\to-\frac{1}{2}} = -\mu_B B \end{cases}$$

$$\begin{cases} E_{\frac{1}{2}\to\frac{1}{2}} = -\frac{1}{3}\mu_B B \\ E_{-\frac{1}{2}\to-\frac{1}{2}} = -\frac{1}{3}\mu_B B \end{cases}$$

Problem 5.10.

Problem 5.11.

Problem 5.12.

(a) We are going to think of every quantity here as a purely classical one. The inversion operator we donote with i:

$$i\left(\mathbf{v}\right) = i\left(\frac{d\mathbf{r}}{dt}\right) = -\frac{d\mathbf{r}}{dt} = -\mathbf{v} \implies \text{polar vector}$$
$$i\left(\mathbf{p}\right) = i\left(m\mathbf{v}\right) = -\mathbf{p} \implies \text{polar vector}$$
$$i\left(\nabla\right) = i\left(\frac{\partial}{\partial\mathbf{r}}\right) = -\frac{\partial}{\partial\mathbf{r}} = -\nabla \implies \text{polar vector}$$
$$i\left(\mathbf{l}\right) = i\left(\mathbf{r}\times\mathbf{p}\right) = \mathbf{r}\times\mathbf{p} = \mathbf{l} \implies \text{axial vector}$$
$$i\left(\mathbf{F}\right) = -\mathbf{F} \implies \text{polar vector}$$
$$i\left(\mathbf{E}\right) = -\mathbf{E} \implies \text{polar vector}$$
$$i\left(\mathbf{B}\right) = \mathbf{B} \implies \text{axial vector}$$
$$i\left(\mathbf{A}\right) = -\mathbf{A} \implies \text{polar vector}$$
$$i\left(\mathbf{m}\right) = \mathbf{m} \implies \text{axial vector}$$

Where by $\mathbf{m}$ is denoted magnetic dipole moment.
(b) We can write the hamiltonian approximately as:

$$H = \underbrace{\sum_{ij}{}^{'} \frac{A_{ij}}{|r_{ij}|}}_{\text{Coulomb interaction}} + \underbrace{\lambda \sum_i \mathbf{l}_i \cdot \mathbf{s}_i}_{\text{spin-orbit coupling}} + \underbrace{\sum_{ij}{}^{'} \left(\frac{\mathbf{m}_i \cdot \mathbf{m}_j}{r_{ij}^3} - 3 \frac{(\mathbf{m}_i \cdot \mathbf{r}_{ij})(\mathbf{m}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right)}_{\text{spin-spin coupling}} + \underbrace{\sum_i \mathbf{B} \cdot (c_{1i}\mathbf{l}_i + c_{2i}\mathbf{s}_i)}_{\text{magnetic field}}$$

The Coulomb interaction is unaffected by inversion of coordinates, because it depends only on the relative distance. As for the spin-orbit interaction we have:

$$i (\mathbf{l}_i \cdot \mathbf{s}_i) = \mathbf{l}_i \cdot \mathbf{s}_i$$

Thus it is unaffected. For the spin orbit interaction the relative distance stays the same after inversion, the magnetic moments also do, and the two polar vectors $\mathbf{r}_{ij}$ take a minus, but the two minus signs cancel each other. Similarly the energy from interaction with the magnetic field is also unaffected because $\mathbf{B}, \mathbf{l}, \mathbf{s}$ are axial vectors an neither of them changes their sign.
From this we conclude that the hamiltonian is invariant under inversion.
(c) Now let us look at what happens if the spin-orbit interaction were to be:

$$i (\mathbf{r} \cdot \mathbf{s}) = (-\mathbf{r}) \cdot \mathbf{s} = -\mathbf{r} \cdot \mathbf{s}$$

Thus we can see that the conclusion from (b) would not hold if the spin-orbit interaction were to be such.

Problem 5.13.

This time we consider only time inversion (including time inversion of fields). We thus have:

$$\begin{aligned}
T(\mathbf{v}) &= i_t \left(\frac{d\mathbf{r}}{dt} \right) = -\frac{d\mathbf{r}}{dt} = -\mathbf{v} \\
T(\mathbf{p}) &= -\mathbf{p} \\
T(\nabla) &= \nabla \\
T(\mathbf{l}) &= T(\mathbf{r} \times \mathbf{p}) = \mathbf{r} \times (-\mathbf{p}) = -\mathbf{l} \\
T(\mathbf{F}) &= \mathbf{F} \\
T(\mathbf{E}) &= \mathbf{E} \\
T(\mathbf{B}) &= -\mathbf{B} \\
T(\mathbf{A}) &= -\mathbf{A} \\
T(\mathbf{m}) &= -\mathbf{m}
\end{aligned}$$

One can get a feeling for each of these results by thinking classically in all of these cases.

Problem 5.14.

Chapter 6

Problem 6.1.

We have to calculate $\langle\Psi|\frac{e^2}{|\mathbf{r}-\mathbf{x}|}|\Psi\rangle$, where $\Psi = Ne^{-\alpha r}$. First we find the normalization factor:

$$\langle\Psi|\Psi\rangle = 4\pi N^2 \int_0^\infty r^2 e^{-2\alpha r} dr = \frac{8\pi N^2}{(2\alpha)^3} = 1 \implies N^2 = \frac{(2\alpha)^3}{8\pi} \qquad \left(\int_0^\infty dx\ x^n e^{-ax} = \frac{\Gamma(n+1)}{a^{n+1}}\right)$$

Now we can calculate the product where the space variables of the wavefunctions are doneted by $\mathbf{x}$:

$$\langle\Psi|\frac{e^2}{|\mathbf{r}-\mathbf{x}|}|\Psi\rangle = N^2 e^2 \int_0^\infty dx \int_0^{2\pi} d\phi \int_0^\pi d\left(-\cos\theta\frac{2rx}{2rx}\right) \frac{x^2 e^{-2\alpha x}}{\sqrt{r^2+x^2-2rx\cos\theta}} =$$

$$= 2\pi e^2 N^2 \int_0^\infty dx\ xe^{-2\alpha x}\frac{r+x-|r-x|}{r} = 4\pi e^2 N^2 \left(\int_0^r dx\ \frac{x^2 e^{-2\alpha x}}{r} + \int_r^\infty dx\ xe^{-2\alpha x}\right) =$$

$$= 4\pi e^2 N^2 \left(\frac{\partial^2}{\partial\alpha^2}\left(\frac{1}{4r}\int_0^r dx\ e^{-2\alpha x}\right) - \frac{1}{2}\frac{\partial}{\partial\alpha}\left(\int_r^\infty dx\ e^{-2\alpha x}\right)\right) =$$

$$= 4\pi e^2 N^2 \left(\frac{\partial^2}{\partial\alpha^2}\left(\frac{1}{8r\alpha}\right) - \frac{\partial^2}{\partial\alpha^2}\left(\frac{e^{-2\alpha x}}{8r\alpha}\right) - \frac{\partial}{\partial\alpha}\left(\frac{e^{-2\alpha r}}{4\alpha}\right)\right) =$$

$$= 4\pi e^2 N^2 \left(\frac{1}{4r\alpha^3} - \frac{re^{-2\alpha r}}{2\alpha} - \frac{e^{-2\alpha r}}{2\alpha^2} - \frac{e^{-2\alpha r}}{4\alpha^3 r} + \frac{re^{-2\alpha r}}{2\alpha} + \frac{e^{-2\alpha r}}{4\alpha^2}\right) = 4\pi e^2 \frac{(2\alpha)^3}{8\pi}\left(\frac{1}{4r\alpha^3} - \frac{e^{-2\alpha r}}{4\alpha^2} - \frac{e^{-2\alpha r}}{4\alpha^3 r}\right) =$$

$$= e^2\left(\frac{1}{r} - \frac{e^{-2\alpha r}(1+\alpha r)}{r}\right)$$

Thus we can now calculate the effective potential energy the second electron experiences by including the interaction with the nucleus:

$$U_{eff}(r) = \frac{-2e^2}{r} + \frac{e^2}{r}\left(1-(1+\alpha r)e^{-2\alpha r}\right) = -\frac{e^2}{r}\left(1+(1+\alpha r)e^{-2\alpha r}\right)$$

Problem 6.2.

(a) We have to calculate the total energy of the electron in an effective field that was obtained in **Problem 6.1.** with wavefunction $\psi = N' e^{-\alpha' r}$. As N' is a normalization costant we calculate it the same way as in the previous problem and it has the same form as N, but we replace α by α'.

$$\langle\psi| H |\psi\rangle = \underbrace{\langle\psi|\left(-\frac{\hbar^2}{2m}\nabla^2\right)|\psi\rangle}_{I_1} + \underbrace{\langle\psi| U_{eff} |\psi\rangle}_{I_2}$$

We calculate first I_1:

$$I_1 = -\frac{\hbar^2}{2m}\int dV \psi^* \nabla^2 \psi = -\frac{\hbar^2}{2m}\frac{(2\alpha')^3}{8\pi}\int_0^\infty 4\pi r^2 dr\ e^{-\alpha' r}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\left(e^{-\alpha' r}\right)\right) =$$

$$= -\frac{\hbar^2}{2m}\frac{(2\alpha')^3}{2}\int_0^\infty dr\left(\alpha'^{\,2} r^2 e^{-2\alpha' r} - 2r\alpha' e^{-2\alpha' r}\right) =$$

$$= -\frac{\hbar^2}{2m}\frac{(2\alpha')^3}{2}\left(\frac{2\alpha'^{\,2}}{(2\alpha')^3} - \frac{2\alpha'}{(2\alpha')^2}\right) = \frac{\hbar^2\alpha'^{\,2}}{2m}$$

And for I_2 we have:

$$I_2 = \int dV \psi^*\ U_e f f \psi = -4\pi e\frac{(2\alpha')^3}{8\pi}\int_0^\infty dr\ r^2 e^{-2\alpha' r}\frac{1+(1+\alpha r)e^{-2\alpha r}}{r} =$$

$$= -e\frac{(2\alpha')^3}{2}\int_0^\infty dr\left(re^{-2\alpha' r} + re^{-2(\alpha+\alpha')r} + \alpha r^2 e^{-2(\alpha+\alpha')}\right) =$$

$$= -e\alpha' - \frac{e^2\alpha'^{\,3}}{(\alpha+\alpha')^2} - \frac{e^2\alpha\alpha'^{\,3}}{(\alpha+\alpha')^3}$$

Thus we can write the energy as a function:

$$E\left(\alpha,\alpha'\right)=\frac{\hbar^{2}\alpha'^{\,2}}{2m}-e\alpha'-\frac{e^{2}\alpha'^{\,3}}{\left(\alpha+\alpha'\right)^{2}}-\frac{e^{2}\alpha\alpha'^{\,3}}{\left(\alpha+\alpha'\right)^{3}}$$

(b) We take the partial derivative with respect to α we have:

$$\partial_{\alpha'}E\left(\alpha,\alpha'\right)=\frac{\hbar^{2}\alpha'}{m}-e^{2}\left(1+\frac{3\alpha'^{\,2}}{\left(\alpha+\alpha'\right)^{2}}-\frac{2\alpha'^{\,3}}{\left(\alpha+\alpha'\right)^{3}}+\frac{3\alpha\alpha'^{\,2}}{\left(\alpha+\alpha'\right)^{3}}-\frac{3\alpha\alpha'^{\,3}}{\left(\alpha+\alpha'\right)^{4}}\right)$$

From symmetry considerations we set $\alpha=\alpha'$ and for the minimum we equate it to 0:

$$\partial_{\alpha'}E\left(\alpha,\alpha\right)=\frac{\hbar^{2}\alpha}{m}-e\left(1+\frac{3}{4}-\frac{2}{8}+\frac{3}{8}-\frac{3}{16}\right)$$

$$\Longrightarrow\ \alpha_{min}=\frac{27}{16}\frac{e^{2}m}{\hbar^{2}}$$

And from this we obtain:

$$E\left(\alpha_{min},\alpha_{min}\right)=\frac{\hbar^{2}\alpha_{min}^{2}}{2m}-e^{2}\alpha_{min}\left(1+\frac{1}{4}+\frac{1}{8}\right)=\alpha_{min}\left(\frac{\hbar^{2}}{2m}\alpha_{min}-\frac{11}{8}e^{2}\right)=$$
$$=-\frac{27}{16}\frac{17}{32}\frac{e^{4}m}{\hbar^{2}}=-\frac{27}{8}\frac{17}{32}Ry\approx 1.79Ry$$

This result agrees quite well with the experimental value.
(c) Now if we first set $\alpha=\alpha'$ and then find the minimum we have:

$$E\left(\alpha,\alpha\right)=\frac{\hbar^{2}\alpha^{2}}{2m}-e\alpha-\frac{e^{2}\alpha}{4}-\frac{e^{2}\alpha}{8}=\frac{\hbar^{2}\alpha^{2}}{2m}-\frac{11}{8}e^{2}\alpha$$

Whose minimum is:

$$E_{min}=-\frac{121}{2\cdot 64}\frac{e^{4}m}{\hbar^{2}}=-\frac{121}{64}Ry\approx -1.89Ry$$

The explanation for the discrepency is that
(d) We have to calculate the expected value of the Hamiltonian $H=-\frac{\hbar^{2}}{2m}\nabla_{1}^{2}-\frac{\hbar^{2}}{2m}\nabla_{2}^{2}-\frac{2e^{2}}{r_{1}}-\frac{2e^{2}}{r_{2}}+\frac{e^{2}}{|\mathbf{r}_{1}-\mathbf{r}_{2}|}$. Some of the terms we can readily write down:

$$E_{atom}=\left\langle\psi_{1}\psi_{2}\right|\frac{\hbar^{2}}{2m}\nabla_{1}^{2}+\frac{\hbar^{2}}{2m}\nabla_{2}^{2}-\frac{2e^{2}}{r_{1}}-\frac{2e^{2}}{r_{2}}+\frac{e^{2}}{|\mathbf{r}_{1}-\mathbf{r}_{2}|}\left|\psi_{1}\psi_{2}\right\rangle=$$
$$=2\frac{\hbar^{2}\alpha^{2}}{2m}-4e^{2}\alpha+e^{2}\underbrace{\left\langle\psi_{1}\psi_{2}\right|\frac{1}{|\mathbf{r}_{1}-\mathbf{r}_{2}|}\left|\psi_{1}\psi_{2}\right\rangle}_{I}$$

Before calculating I, let us note that $|\mathbf{r}_{1}-\mathbf{r}_{2}|=|\mathbf{r}_{2}-\mathbf{r}_{1}|$, thus instead of integrating both r_{1} and r_{2} from 0 to ∞, we will integrate r_{2} from 0 to r_{1} and integrate r_{1} from 0 to ∞ and take a factor of two infront of the integral:

$$I = 2N^4 \int d^3r_1 \int_0^{r_1} \int_0^{\pi} \int_0^{2\pi} r_2^2 dr_2 \ \sin\theta d\theta \ d\phi \ \frac{e^{-2\alpha(r_1+r_2)}}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta}} =$$
$$= 2\frac{(2\alpha)^6}{(8\pi)^2} 2\pi \int d^3r_1 \int_0^{r_1} \int_0^{\pi} r_2 dr_2 d\left(-r_2\cos\theta\frac{2r_1}{2r_1}\right) \frac{e^{-2\alpha(r_1+r_2)}}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta}} =$$
$$= \frac{(2\alpha)^6}{16\pi} \int d^3r_1 e^{-2\alpha r_1} \int_0^{r_1} dr_2 \ r_2 e^{-2\alpha r_2} \frac{r_1+r_2-|r_1-r_2|}{r_1} =$$
$$= \frac{(2\alpha)^6}{8\pi} \int d^3r_1 \frac{e^{-2\alpha r_1}}{r_1} \int_0^{r_1} dr_2 \ r_2^2 e^{-2\alpha r_2} = \frac{(2\alpha)^6}{4\cdot 8\pi} \int d^3r_1 \frac{e^{-2\alpha r_1}}{r_1} \frac{\partial^2}{\partial\alpha^2}\left(\int_0^{r_1} dr_2 \ e^{-2\alpha r_2}\right) =$$
$$= \frac{(2\alpha)^6}{32\pi} \int_0^{\infty} 4\pi r_1^2 dr_1 \frac{e^{-\alpha r_1}}{r_1} \frac{\partial^2}{\partial\alpha^2}\left(\frac{1-e^{-2\alpha r_1}}{2\alpha}\right) =$$
$$= \frac{(2\alpha)^6}{8} \int_0^{\infty} dr_1 \ r_1 e^{-2\alpha r_1} \left(\frac{1}{\alpha^3} - \frac{4r_1^2 e^{-2\alpha r_1}}{2\alpha} - \frac{4r_1 e^{-2\alpha r_1}}{2\alpha^2} - \frac{e^{-2\alpha r_1}}{\alpha^3}\right) =$$
$$= \frac{64\alpha^6}{8} \int_0^{\infty} dr_1 \ \left(r_1\frac{e^{-2\alpha r_1}}{\alpha^3} - 2r_1^3\frac{-4\alpha r_1}{\alpha} - 2r_1^2\frac{e^{-4\alpha r_1}}{\alpha^2} - r_1\frac{e^{-4\alpha r_1}}{\alpha^3}\right) =$$
$$= 8\alpha^6\left(\frac{1}{4\alpha^5} - \frac{2\cdot 6}{4^4\alpha^5} - \frac{2\cdot 2}{4^3\alpha^5} - \frac{1}{4^2\alpha^5}\right) = 8\alpha^6\frac{5}{64\alpha^5} = \frac{5}{8}\alpha$$

Now we can calculate the total binding energy:

$$E_{atom} = \frac{\hbar^2\alpha^2}{m} - 4e^2\alpha + \frac{5}{8}e^2\alpha = \frac{\hbar^2}{m}\alpha^2 - \frac{27}{8}e^2\alpha = \frac{\hbar^2}{m}\frac{e^4m^2}{\hbar^4}\left(\frac{27}{16}\right)^2 - \frac{27}{8}\frac{e^4m}{\hbar^2}\frac{27}{16} =$$
$$= -\left(\frac{27}{16}\right)^2\frac{e^4m}{\hbar^2} = -\frac{27^2}{8\cdot 16}Ry = -\frac{729}{128}Ry \approx -5.69Ry$$

From this we obtain the binding energy of the second electron as:

$$E_{second} = E_{atom} - 4Ry = -1.69Ry$$

Problem 6.3.

Let us try a solution of the form $\varphi = A^{-2\alpha r} + \frac{B}{r}e^{-2\alpha r}$:

$$\Delta\varphi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi}{\partial r}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(-2\alpha A r^2 e^{-2\alpha r} - Be^{-2\alpha r}(1+2\alpha r)\right) =$$
$$= e^{-2\alpha r}\left(4\alpha^2 A + \frac{1}{r}\left(4\alpha^2 B - 4\alpha A\right)\right) = -4\pi\cdot e\frac{2\alpha^3}{\pi}e^{-2\alpha r} = -4\alpha^3(Z-1)e^{-2\alpha r}$$

From this we obtain our coefficients:

$$\begin{cases} A = -e\alpha(Z-1) \\ B = -e(Z-1) \end{cases}$$

Which gives us the following potential:

$$U = -\frac{e^2}{r} + e\phi = -\frac{e^2}{r} - \frac{(Z-1)e^2(1+\alpha r)e^{-2\alpha r}}{r} = -\frac{e^2}{r}\underbrace{\left(1+(Z-1)(1+\alpha r)e^{-2\alpha r}\right)}_{Z_p}$$

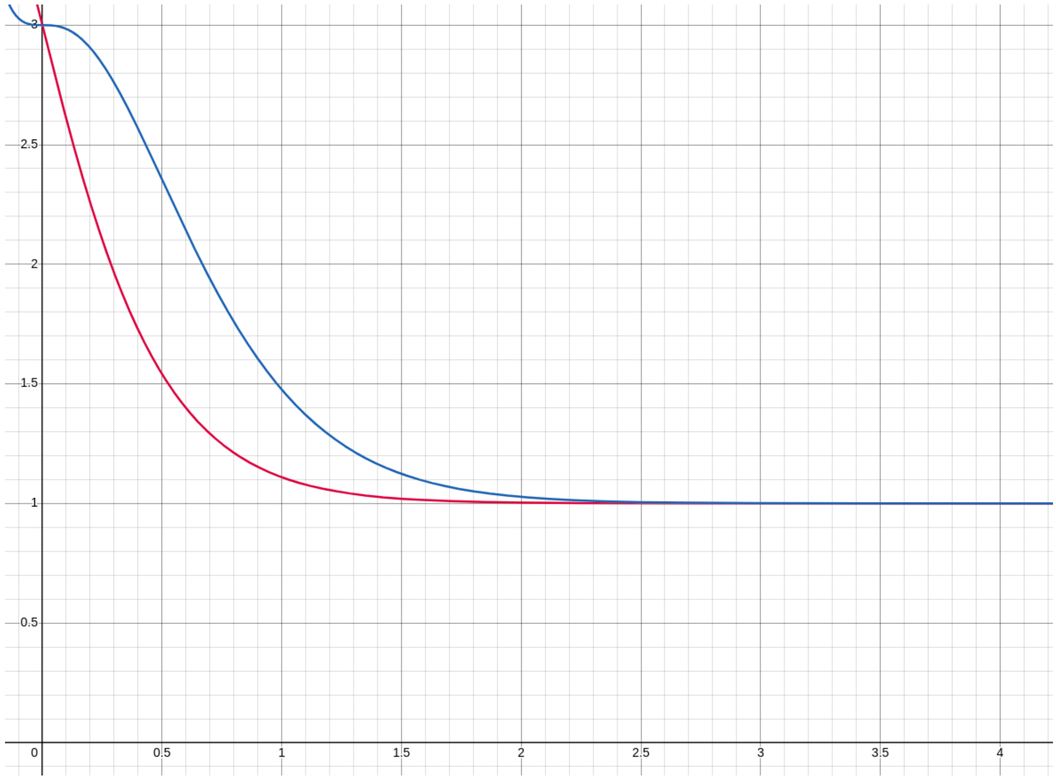
(b) Now that we have:

$$Z_p(r) = 1 + (Z-1)(1+\alpha r)e^{-2\alpha r}$$

And we can calculate:

$$Z_f(r) = Z_p(r) - r\frac{dZ_p}{dr} = 1 + (Z-1)(1+\alpha r)e^{-2\alpha r} - r(Z-1)\left(\alpha - 2\alpha - 2\alpha^2 r\right)e^{-2\alpha r} =$$
$$= 1 + (Z-1)\left(1 + 2\alpha r + 2\alpha^2 r^2\right)e^{-2\alpha r}$$

Now we plot the function with r measured in Bohr's radius. I the plot the red line represents Z_p and the blue line represents Z_f.



Problem 6.4.

We have the following wavefunction $\psi_{2p} = Are^{-br}Y_1^m(\theta,\phi)$, where A is a real parameter. First we calculate the normalization factor:

$$\langle \psi_{2p} | \psi_{2p} \rangle = A^2 \int_0^\infty r^2 dr\; r^2 e^{-2br} \int_0^\pi \int_0^{2\pi} \sin\theta\; d\theta d\phi\; Y_1^{m*} Y_1^m = \frac{24A^2}{(2b)^5} = 1$$

$$\implies A^2 = \frac{4b^5}{3}$$

Now we calculate the energy as a function of the parameter b:

$$E(b) = \underbrace{\langle \psi_{2p} | -\frac{\hbar^2}{2m}\nabla^2 | \psi_{2p} \rangle}_{I_1} + \underbrace{\langle \psi_{2p} | -\frac{e^2}{r}\left(1 + (Z-1)(1+\alpha r)e^{-2\alpha r}\right) | \psi_{2p} \rangle}_{I_2}$$

Remembering that Y_l^m is an eigenfunction of the Laplacian, we can calculate directly the first integral:

$$\begin{aligned}
I_1 &= -\frac{\hbar^2 A^2}{2m}\int d^3r\; re^{-br} Y_1^{m*} \nabla^2 \left(re^{-br}Y_1^m\right) = \\
&= -\frac{\hbar^2 A^2}{2m}\int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin\theta\; drd\theta d\phi\; re^{-br} Y_1^{m*}\left(\nabla_r^2\left(re^{-br}\right)Y_1^m + re^{-br}\nabla^2_{\theta\phi}\left(Y_1^m\right)\right) = \\
&= -\frac{\hbar^2 A^2}{2m}\left(\int_0^\pi \int_0^{2\pi} d\theta d\phi\; \sin\theta Y_1^{m*} Y_1^m\right)\left(\int_0^\infty dr\; re^{-br}\left(\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\left(re^{-br}\right)\right)\right) + (-2)\, re^{-2br}\right) = \\
&= -\frac{\hbar^2 A^2}{2m}\int_0^\infty dr\; re^{-br}\left(b^2 r^3 e^{-br} - 3br^2 e^{-br} + 2re^{-br} - br^2 e^{-br} - 2re^{-br}\right) = \\
&= -\frac{\hbar^2 A^2}{2m}\int_0^\infty dr\left(b^2 r^4 e^{-2br} - 4br^3 e^{-2br}\right) = -\frac{\hbar^2 A^2}{2m}\left(b^2 \frac{24}{(2b)^5} - 4b\frac{6}{(2b)^4}\right) = \\
&= -\frac{\hbar^2 A^2}{2m}\left(-\frac{3}{4b^3}\right) = \frac{\hbar^2 b^2}{2m}
\end{aligned}$$

Now we calculate the second integral:

$$
\begin{aligned}
I_2 &= -e^2 A^2 \int_0^\infty dr\ r^2\ re^{-br} \frac{\left(1 + (Z-1)(1+\alpha r) e^{-2\alpha r}\right)}{r}\ re^{-br} \int_0^\pi \int_0^{2\pi} \sin\theta\ d\theta d\phi\ Y_1^{m*} Y_1^m = \\
&= -e^2 A^2 \int_0^\infty dr r^3 e^{-2br} \left(1 + (Z-1)(1+\alpha r) e^{-2\alpha r}\right) = \\
&= -e^2 A^2 \int_0^\infty dr \left(r^3 e^{-2br} + (Z-1) r^3 e^{-2(\alpha+b)r} + \alpha (Z-1) r^4 e^{-2(\alpha+b)r}\right) = \\
&= -e^2 \frac{4b^5}{3} \left(\frac{6}{(2b)^4} + (Z-1)\frac{6}{(2(\alpha+b))^4} + \alpha(Z-1)\frac{24}{(2(\alpha+b))^5}\right) = \\
&= -e^2 \frac{4b^5}{3} \left(\frac{3}{8b^4} + (Z-1)\frac{3}{8(\alpha+b)^4} + \frac{3(Z-1)\alpha}{4(\alpha+b)^5}\right) = \\
&= -e^2 \left(\frac{b}{2} + \frac{(Z-1) b^5}{2(\alpha+b)^4} + \frac{(Z-1)\alpha b^5}{(\alpha+b)^5}\right)
\end{aligned}
$$

Thus for the energy we have:

$$
E(b) = \frac{\hbar^2 b^2}{2m} - e^2 \left(\frac{b}{2} + \frac{(Z-1) b^5}{2(\alpha+b)^4} + \frac{(Z-1)\alpha b^5}{(\alpha+b)^5}\right)
$$

Now we take the derivative with respect to b to search for extrema:

$$
\frac{dE}{db} = 0 = e^2 \left(\frac{\hbar^2 b}{me^2} - \left(\frac{1}{2} + \frac{(Z-1)\left(5\alpha b^4 + b^5\right)}{2(\alpha+b)^5} + \frac{5(Z-1)\alpha^2 b^4}{(\alpha+b)^6}\right)\right)
$$

In order to find the optimal value of b we will change the variable and write $b = \alpha x$. We then remember that $a_0 = \frac{\hbar^2}{me^2}$ and then use the fact that $\alpha = \frac{2}{a_0}$, where a_0 is Bohr's radius. From this follows a great simplification:

$$
\begin{aligned}
0 &= \frac{\hbar^2 \alpha x}{me^2} - \left(\frac{1}{2} + \frac{(Z-1)\left(5x^4 + x^5\right)}{2(1+x)^5} + \frac{5(Z-1)x^4}{(1+x)^6}\right) = \\
&= 2x - \left(\frac{1}{2} + \frac{x^4(5+x)}{(1+x)^5} + \frac{10x^4}{(1+x)^6}\right)
\end{aligned}
$$

From which we obtain the following equation that may be solved using successive approximations starting for example from $x = \frac{1}{4}$:

$$
x = \frac{1}{4} + \frac{x^4(5+x)}{2(1+x)^5} + \frac{5x^4}{(1+x)^6}
$$

The solution is $x \approx 0.25936$, which yields $b_{min} = \frac{0.518872}{a_0}$, which if we plug back into the equation for the energy:

$$
E(b_{min}) \approx -0.254 Ry
$$

From this we see that the value agrees quite well with the experimental one of $-0.260Ry$.

Problem 6.5.

We have to calculate:

$$
\delta = \left(L + \frac{1}{2}\right) \xi(2p) = \frac{3}{2} \frac{\hbar^2 e^2}{2m^2 c^2} \left\langle \frac{Z_f}{r^3} \right\rangle
$$

Where we have we only need to calculate the:

$$\begin{aligned}
\left\langle \frac{Z_f}{r^3} \right\rangle &= \int r^2 \sin\theta d\Omega dr A^2 r^2 e^{-2br} Y_1^{m*} Y_1^m \frac{1+(Z-1)\left(1+2\alpha r+2\alpha^2 r^2\right)e^{-2\alpha r}}{r^3} = \\
&= A^2 \int dr \left(re^{-2br} + (Z-1)\left(r + 2\alpha r^2 + 2\alpha^2 r^3\right) e^{-2(\alpha+b)r} \right) = \\
&= A^2 \left(\frac{1}{(2b)^2} + 2\left(\frac{1}{4(\alpha+b)^2} + \frac{4\alpha}{8(\alpha+b)^3} + \frac{12\alpha^2}{16(\alpha+b)^4} \right) \right) = \\
&= \frac{4}{3} b^5 \left(\frac{1}{4b^2} + \frac{2}{(\alpha+b)^2} + \frac{\alpha}{(\alpha+b)^3} + \frac{3\alpha^2}{2(\alpha+b)^4} \right) = \\
&= \frac{4}{3} b^3 \left(\frac{1}{4} + \frac{2\cdot 0.259436^2}{1.259436^2} + \frac{0.259436^2}{1.259436^3} + \frac{3\cdot 0.259436^2}{2\cdot 1.259436^4} \right) = \\
&= \frac{4}{3} \frac{0.518872^3}{a_0^3} \left(\frac{1}{4} + \frac{2\cdot 0.259436^2}{1.259436^2} + \frac{0.259436^2}{1.259436^3} + \frac{3\cdot 0.259436^2}{2\cdot 1.259436^4} \right) \approx \\
&\approx \frac{0.05425}{a_0^3}
\end{aligned}$$

Which yields:

$$\delta = \frac{\hbar^2 e^2}{2m^2c^2} \frac{0.05425}{a_0^3} \approx 0.317 \text{ cm}^{-1} \approx 0.32 \text{ cm}^{-1}$$

The result is quite close to the true one of 0.34 cm^{-1}.

Problem 6.6.

First we compute:

$$\begin{aligned}
\left\langle \frac{1}{r^3} \right\rangle &= \int dV \psi_{2p}^* \frac{1}{r^3} \psi_{2p} = \int r^2 \sin\theta \; dr d\theta d\phi \; \frac{1}{r^3} A^2 r^2 e^{-2br} Y_1^{m*} Y_1^m = \\
&= A^2 \int_0^\infty re^{-2br} = \frac{4b^5}{3} \frac{1}{4b^2} = \frac{b^3}{3} = \frac{1}{3} \frac{(0.518872)^3}{a_0^3}
\end{aligned}$$

Now we can calculate Z_i:

$$Z_i = \frac{\left\langle \frac{Z_f}{r^3} \right\rangle}{\left\langle \frac{1}{r^3} \right\rangle} = \frac{\frac{0.05425}{a_0^3}}{\frac{1}{3}\frac{(0.518872)^3}{a_0^3}} = \frac{3\cdot 0.05425}{(0.518872)^3} \approx 1.17$$

Problem 6.7.

$M_L \backslash M_S$	1	0	-1
4		$(2^+, 2^-)$	
3	$(2^+, 1^+)$	$(2^+, 1^-)$, $(2^-, 1^+)$	$(2^-, 1^-)$
2	$(2^+, 0^+)$	$(2^+, 0^-)$, $(1^+, 1^-)$, $(2^-, 0^+)$	$(2^-, 0^-)$
1	$(2^+, -1^+)$, $(1^+, 0^+)$	$(2^+, -1^-)$, $(2^-, -1^+)$, $(1^+, 0^-)$, $(1^-, 0^+)$	$(2^-, -1^-)$, $(1^-, 0^-)$
0	$(2^+, -2^+)$, $(1^+, -1^+)$	$(2^+, -2^-)$, $(-2^+, 2^-)$, $(1^+, -1^-)$, $(1^-, -1^+)$, $(0^+, 0^-)$	$(2^-, -2^-)$, $(1^-, -1^-)$
-1	$(-2^+, +1^+)$, $(-1^+, 0^+)$	$(-2^+, +1^-)$, $(-2^-, -1^+)$, $(-1^+, 0^-)$, $(-1^-, 0^+)$	$(-2^-, +1^-)$, $(-1^-, 0^-)$
-2	$(-2^+, 0^+)$	$(-2^+, 0^-)$, $(-1^+, -1^-)$, $(-2^-, 0^+)$	$(-2^-, 0^-)$
-3	$(-2^+, -1^+)$	$(-2^+, -1^-)$, $(-2^-, -1^+)$	$(-2^-, -1^-)$
-4		$(-2^+, -2^-)$	

Problem 6.8.

Problem 6.9.

Problem 6.10.

Problem 6.11.

Problem 6.12.

The Wigner-Eckart theorem tells us that:

$$\left\langle \Phi_{j''}^{m''} \middle| O_j^m \middle| \Psi_{j'}^{m'} \right\rangle \propto C_{jj'}\left(j''m''; mm'\right)$$

There can be a nonzero matrix element for transition between two different states if the Clebsch-Gordon coefficient is not 0. The position operator $\mathbf{r}$ has $j = 1$ and possible values for $m = -1, 0, 1$. But $\mathbf{r}$ does not act on the spin part of the wave function but acts on the orbital momentum. Due to the fact that they can be expressed in terms of spherical harmonics that have definite parity and $\mathbf{r}$ itself has an odd parity then, another condition for transition between two states is that they differ by $\Delta l = \pm 1$, as then we switch parity from one state to the other.

Finally we can write transition elements as:

$$\left\langle L_{j''}^{m''} \middle| r_m^{(1)} \middle| l_{j'}^{m'} \right\rangle \propto C_{jj'}\left(j''m''; mm'\right)\left(\delta_{l,L-1} + \delta_{l,L+1}\right)$$

And we have:

$$\langle \Phi | \mathbf{E} \cdot \mathbf{r} | \Psi \rangle = \mathbf{E} \cdot \left(\langle \Phi | \mathbf{r} | \Psi \rangle\right)$$

(a) We have:

$$\left\langle {}^3D_2 \right| r_m^{(1)} \left| {}^3P_0 \right\rangle \propto C_{1,0}\left(2, m''; mm'\right)\left(\delta_{1,2-1} + \delta_{1,2+1}\right)$$

Transition $2p^2\ {}^3P_0 \to 2p3d\ {}^3D_2$ is forbidden as $2 \neq 0 + 1$.
Note: This can be physically interpreted as the photon has spin one, the angular momentum of the state can change by no more than 1. Thus this expresses the conservation of angular momentum for one photon transitions.
(b) We have:

$$\left\langle {}^3P_1 \right| r_m^{(1)} \left| {}^3P_0 \right\rangle \propto C_{1,0}\left(1, m''; mm'\right)\left(\delta_{1,1-1} + \delta_{1,1+1}\right)$$

Transition $2p^2\ {}^3P_0 \to 2s2p\ {}^3P_1$ is forbidden.
(c) We have:

$$\left\langle {}^3S_1 \right| r_m^{(1)} \left| {}^3P_0 \right\rangle \propto C_{1,0}\left(1, m''; mm'\right)\left(\delta_{1+1,0} + \delta_{1-1,0}\right)$$

Transition $2p^2\ {}^3P_0 \to 2s3s\ {}^3S_1$ is allowed as we there is both a nonzero delta coefficient and there are non-zero Clebsch-Gordon coefficients.
(d) We have:

$$\left\langle {}^1P_1 \right| r_m^{(1)} \left| {}^3P_0 \right\rangle \propto C_{1,0}\left(1, m''; mm'\right)\left(\delta_{1,1-1} + \delta_{1,1+1}\right)$$

Transition $2p^2\ {}^3P_0 \to 2s2p\ {}^1P_1$ is forbidden.

Problem 6.13.

Problem 6.14.

Chapter 7

Problem 7.1.

Problem 7.2.

Problem 7.3.

Problem 7.4.

Problem 7.5.

Problem 7.6.

Problem 7.7.

Problem 7.8.

Problem 7.9.

Problem 7.10.

Problem 7.11.

Chapter 8

Problem 8.1.

Rather than me describing how this is done, I think that seeing the steps animated would be the best. So I recommend the following link: `https://www.doitpoms.ac.uk/tlplib/brillouin_zones/zone_construction.php`

Problem 8.2.

Problem 8.3.

Problem 8.4.

Problem 8.5.

Problem 8.6.

Problem 8.7.

Problem 8.8.

Problem 8.9.