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Crystal Field Effects on Multiplets Observed in Open d- and f- shells

Master's Thesis

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CHAPTER 1

Abstract

The subject of the thesis is to study a crystal field and spin-orbit coupling effects on multiplets observed in open d- and f-shells. The Coulomb interaction is considered by building the electrostatic matrix, where the required Gaunt coefficient are calculated recursively. Continuous fractions are used to produce Gaunt coefficients in the form of square roots of rational numbers to verify them. L-S coupling between orbital and spin angular momenta is assumed. Due to the spherical symmetry of the Coulomb potential, orbital and spin angular momenta are conserved separately. The corresponding quantum numbers are used to classify the eigenstates of the electrostatic matrix. These are compared with the eigenstates of simplified approximations to the electrostatic matrix. Then a cubic or tetragonal crystal field is introduced to electrostatic Hamiltonian and the interplay of Hund's rule and crystal-field splitting is studied. Finally spin-orbit coupling is added.

Keywords: *Multiplets*, *Gaunt Co-efficients*, *Coulomb tensor*, *Model Hamiltonian*, *Crystal-field splitting*

C H A P T E R 2

Many Body Problem

2.1. The Hydrogen Atom

2.1.1. Schrödinger equation for the hydrogen atom

The simplest one-electron system that we consider is that of atomic hydrogen [1]. The hydrogen atom comprises of one electron, and the nucleus contains a proton. Both these particles have a set of co-ordinates associated with them: (x_e, y_e, z_e) for the electron and

(x_p, y_p, z_p) for the proton. The wave-function depends on all six co-ordinates. The complexity is introduced by the fact that the electron and the proton cannot be treated independently, as their co-ordinates are linked through the electrostatic potential between the electron and the proton. This is resolved by choosing an appropriate co-ordinate system, which will reduce the number of independent co-ordinates. We work in the SI units for a while. The Hamiltonian for this system can be written as

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + V\left(|\mathbf{r}_e - \mathbf{r}_p|\right) \tag{2.1}$$

where the Laplacian for the electron is defined as

$$\nabla_e^2 \equiv \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \tag{2.2}$$

and similarly for the proton. The electrostatic interaction between the electron and the proton is given by

$$V\left(|\mathbf{r}_e - \mathbf{r}_p|\right) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_e - \mathbf{r}_p|} \tag{2.3}$$

The eigenenergies and corresponding wave-functions can then be obtained by solving the Schrödinger equation for this Hamiltonian

$$\hat{\mathcal{H}}\psi\left(\mathbf{r}_e, \mathbf{r}_p\right) = E\psi\left(\mathbf{r}_e, \mathbf{r}_p\right) \tag{2.4}$$

The electrostatic interaction is dependent, not on the absolute positions of the electron and the proton, but on the the relative displacement between them. Now we switch to the center of mass co-ordinate system. We define a relative position vector

$$x = x_e - x_p, \quad y = y_e - y_p, \quad z = z_e - z_p \tag{2.5}$$

which would then mean that

$$r = \sqrt{x^2 + y^2 + z^2} = |\mathbf{r}_e - \mathbf{r}_p| \tag{2.6}$$

We need three more co-ordinates to complete the six we originally had. The position of the center of mass ($\mathbf{R}$) is chosen.

$$\mathbf{R} = X\mathbf{i} + Y\mathbf{j} + Z\mathbf{k} = \frac{m_e\mathbf{r}_e + m_p\mathbf{r}_p}{m_e + m_p} \tag{2.7}$$

We need to recast our Hamiltonian in terms of the new co-ordinate vectors $\mathbf{R}$ and $\mathbf{r}$. Using the chain rule for derivatives, after some mathematical manipulation, we find that

$$\frac{1}{m_e}\frac{\partial^2}{\partial x_e^2} + \frac{1}{m_p}\frac{\partial^2}{\partial x_p^2} = \frac{1}{m_e + m_p}\frac{\partial^2}{\partial X^2} + \frac{m_e + m_p}{m_e m_p}\frac{\partial^2}{\partial x^2} \tag{2.8}$$

and similarly for the other two directions. We define the total mass $M = m_e + m_p$ and then a *reduced mass* $\mu = \frac{m_e m_p}{m_e + m_p}$ and rewrite the Hamiltonian as

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r}) \tag{2.9}$$

We now need to solve the Schrödinger equation (2.4) to find the wave-functions and eigenenergies. At this point, we make an ansatz: the wave-function ψ is separable into two parts each dependent on one of the independent co-ordinates i.e.

$$\psi(\mathbf{R}, \mathbf{r}) = \chi(\mathbf{R})\,\varphi(\mathbf{r}) \tag{2.10}$$

We can substitute this into the Schrödinger equation

$$\begin{aligned}
&\left(-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right)\ \chi(\mathbf{R})\,\varphi(\mathbf{r}) = E\,\chi(\mathbf{R})\,\varphi(\mathbf{r}) \\
\Rightarrow\ &-\varphi(\mathbf{r})\left[\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\chi(\mathbf{R})\right] + \chi(\mathbf{R})\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right]\varphi(\mathbf{r}) = E\,\chi(\mathbf{R})\,\varphi(\mathbf{r})
\end{aligned} \tag{2.11}$$

Then we divide the equation by $\chi(\mathbf{R})\,\varphi(\mathbf{r})$ to get

$$-\frac{1}{\chi(\mathbf{R})}\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\,\chi(\mathbf{R}) = E - \frac{1}{\varphi(\mathbf{r})}\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right]\varphi(\mathbf{r}) \tag{2.12}$$

Since the left hand side and the right hand side depend on independent variables $\mathbf{R}$ and $\mathbf{r}$, they can be equal in general, only if they are equal to some constant. Let us denote this constant by E_{CM}, which means that

$$-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\,\chi\left(\mathbf{R}\right) = E_{CM}\,\chi\left(\mathbf{R}\right) \tag{2.13}$$

and

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V\left(\mathbf{r}\right)\right]\varphi\left(\mathbf{r}\right) = E_H\,\varphi\left(\mathbf{r}\right) \tag{2.14}$$

where $E = E_{CM} + E_H$

The first of these equations (2.13) is clearly just a free particle Schrödinger equation, the wave-functions of which, after normalisation, are given by

$$\chi\left(\mathbf{R}\right) = \frac{1}{\sqrt{\left(2\pi\hbar\right)^3}}\exp\left(i\mathbf{K}\cdot\mathbf{R}\right) \tag{2.15}$$

and the eigenergies are given by

$$E_{CM} = \frac{\hbar^2 K^2}{2M} \tag{2.16}$$

The eigenenergy corresponds to the center of mass of the electron-proton system, and hence gives the energy of the motion of the atom through space. The equation (2.17) describes the motion of the electron and the proton relative to each other *within* the hydrogen atom. This is the equation of greater interest for us. In order to simplify the notation a bit further, we now switch to atomic units (see Appendix A). Since $m_p \gg m_e$, we conclude that $\mu \approx m_e = 1$. In this system of units we can rewrite (2.14) as

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V\left(\mathbf{r}\right)\right]\varphi\left(\mathbf{r}\right) = E_H\,\varphi\left(\mathbf{r}\right) \tag{2.17}$$

To solve for the internal states of the hydrogen atom, we exploit the spherical symmetry of the eigenvalue equation and transform it into spherical co-ordinates. The Laplacian can be written as

$$\nabla_{\mathbf{r}}^{2}=\frac{1}{r^{2}}\frac{\partial}{\partial r}\left(r^{2}\frac{\partial}{\partial r}\right)+\frac{1}{r^{2}}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^{2}\theta}\frac{\partial^{2}}{\partial^{2}\phi}\right] \tag{2.18}$$

We now tackle this problem in two steps. First we introduce the angular momentum operators to look at how the angular dependence of the Schrödinger function can be solved for, and then we deal with the radial part.

2.1.2. Angular momentum operators

We recall from classical mechanics that the angular momentum **L** for a body moving at momentum **p** and located at a position **r** with respect to some origin is defined as

$$\mathbf{L}=\mathbf{r}\times\mathbf{p} \tag{2.19}$$

The quantum mechanical angular momentum operator is defined in analogy to the classical variant as

$$\hat{\mathbf{L}}=\hat{\mathbf{r}}\times\hat{\mathbf{p}}=\mathbf{r}\times(-i\nabla)=-i\mathbf{r}\times\nabla \tag{2.20}$$

Then, the components of the angular momentum will be

$$\begin{aligned}\hat{L}_x&=-i\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\\ \hat{L}_y&=-i\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)\\ \hat{L}_z&=-i\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\end{aligned} \tag{2.21}$$

In the presence of an external field, the angular momentum is, in general, not conserved. Rather, the conservation properties depend on the symmetry of the external field. In our derivation, in the center of mass frame (2.17), we have a centrally symmetric field, and hence all the radial directions are equivalent. Therefore, the angular momentum is conserved.

Starting from the Hermiticity of the position and momentum operators and from the commutation relations between the position and momentum operators, it can be shown that the individual components of the angular momentum operator are Hermitian and that they hold the following commutation relations

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hat{L}_z \qquad \left[\hat{L}_y, \hat{L}_z\right] = i\hat{L}_x \qquad \left[\hat{L}_z, \hat{L}_x\right] = i\hat{L}_y \tag{2.22}$$

It will be useful to transform the angular momentum operators into spherical co-ordinates too. So we substitute $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$ and $z = r\cos\theta$. Using the chain rule for derivatives, we can write that

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi} \tag{2.23}$$

and similarly for the y and z components. After some work, it can be shown that

$$\hat{L}_x = i\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \tag{2.24}$$

$$\hat{L}_y = i\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \tag{2.25}$$

$$\hat{L}_z = -i\frac{\partial}{\partial\phi} \tag{2.26}$$

We can immediately solve equation (2.26) to find the eigenvalues and eigenfunctions of the $\hat{L}_z$ operator. Let the eigenvalues be m and the eigenfunctions be $\Phi\left(\phi\right)$

$$\hat{L}_z\Phi\left(\phi\right) = m\Phi\left(\phi\right) \tag{2.27}$$

The eigenfunctions $\Phi\left(\phi\right)$ are given by $\exp\left(im\phi\right)$. The choice of the z-axis is arbitrary, i.e. we could have chosen the x or the y axis as the polar axis, and then we could have obtained similar results. It is not surprising that the expressions for the x and y components of angular momentum are different from that of the z component, because of the commutation relations between the operators(equation (2.22)).

Another operator we need to consider is the $\hat{\mathbf{L}}^2$. It is simple, but cumbersome, to calculate this operator, but it can be shown that

$$\begin{aligned}\hat{\mathbf{L}}^2 &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \\ &= -\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \\ &= -\nabla^2_{\theta,\phi}\end{aligned} \tag{2.28}$$

We can also write an eigenvalue equation for $\hat{\mathbf{L}}^2$. Since the operator depends on θ and ϕ, we can assume that the eigenfunctions will be functions of both θ and ϕ. So

$$\hat{\mathbf{L}}^2 Y(\theta, \phi) = l(l+1) Y(\theta, \phi) \tag{2.29}$$

The notation $Y(\theta, \phi)$ for the eigenfunctions and $l(l+1)$ for the eigenvalues is pre-emptive. Now $\hat{\mathbf{L}}^2$ has some nice properties. It commutes with each of $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$. That means that $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ have common eigenfunctions. We have already found the eigenfunctions of $\hat{L}_z$ in equation (2.27). The form of the $\hat{L}_z$ operator suggests a separation of the variables θ and ϕ in the eigenfunctions of $\hat{\mathbf{L}}^2$. We anticipate such a separation and make an ansatz

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) \tag{2.30}$$

Substituting this ansatz into the eigenvalue equation, then multiplying throughout by $\sin^2\theta$, dividing by $\Theta(\theta)\Phi(\phi)$ and then rearranging the terms, we get

$$\frac{1}{\Phi(\phi)} \frac{d^2\Phi(\phi)}{d\phi^2} = -l(l+1)\sin^2\theta - \frac{\sin\theta}{\Theta(\theta)} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta(\theta)}{d\theta}\right) \tag{2.31}$$

From equation (2.27) we already know how to find the left hand side of this equation. Substituting and rearranging again, we get

$$\frac{1}{\sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{d}{d\theta}\right)\Theta(\theta) - \frac{m^2}{\sin^2\theta} + l(l+1)\Theta(\theta) = 0 \tag{2.32}$$

The above equation has known solutions, which are the associated Legendre functions $\Theta(\theta) = P_l^m(\cos\theta)$, where P_l^m is defined by the Rodrigues formula

$$P_l^m(x) = \frac{1}{2^l l!}\left(1 - x^2\right)^{\frac{m}{2}} \frac{d^{l+m}}{dx^{l+m}}\left(x^2 - 1\right)^l \tag{2.33}$$

These solutions require that

$$l = 0, 1, 2, 3, \ldots; \qquad -l \leq m \leq +l \quad (\, m \,\epsilon\, \mathbb{Z}\,) \tag{2.34}$$

Thus we now know the eigenvalues and joint eigenfunctions of the $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ operators. Now we note that the operator $\nabla^2_{\theta,\phi}$ is the same as the second term in the Laplacian operator in the Schrödinger equation for the hydrogen atom (2.18), except for a factor of $\frac{1}{r^2}$. Since the first term of the Laplacian in (2.18) is independent of angular co-ordinates, it is easily seen that

$$\left[\nabla^2_{\mathbf{r}}, \nabla^2_{\theta,\phi}\right] = 0 \tag{2.35}$$

Using equation (2.17) and (2.28), we can then write that

$$\left[\hat{\mathbf{L}}^2, \hat{\mathcal{H}}\right] = 0 \tag{2.36}$$

This is a very important result, since this implies that the Hamiltonian can be simultaneously diagonalised with the $\hat{\mathbf{L}}^2$ operator. Further, since we already know the eigenfunctions of $\hat{\mathbf{L}}^2$, they are also eigenfunctions of the Hamiltonian.

The eigenvalue equation for the hydrogen atom (2.17) dictates that

$$\left[-\frac{1}{2}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\nabla^2_{\theta,\phi}\right\} + V\left(\mathbf{r}\right)\right]\varphi\left(\theta,\phi\right) = E_H\ \varphi\left(r,\theta,\phi\right) \tag{2.37}$$

Looking at equation (2.37), it is evident that the function $\varphi\left(r,\theta,\phi\right)$ contains the function $Y\left(\theta,\phi\right)$. This suggests to us that it could be possible to separate the r dependence of the wave function $\varphi\left(\mathbf{r}\right)$ from the angular dependence. Thus, we make a second ansatz

$$\varphi\left(\mathbf{r}\right) = R\left(r\right)Y\left(\theta,\phi\right) \tag{2.38}$$

2.1.3. Radial part of the hydrogen wave-function

We now need to find the radial part of the wave-function $R\left(r\right)$. It will be beneficial if we recast the radial part as

$$\varphi\left(\mathbf{r}\right) = \frac{1}{r}\xi\left(r\right)Y\left(\theta,\phi\right) \tag{2.39}$$

The radial derivatives in (2.18), when applied to the radial part of $\varphi\left(\mathbf{r}\right)$ then become

$$\begin{aligned}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}R(r)\right) &= \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\left(\frac{\xi(r)}{r}\right)\right] \\ &= \frac{1}{r}\frac{\partial^2\xi}{\partial r^2} \end{aligned} \tag{2.40}$$

Then, after substitution into the equation (2.17), the Schrödinger equation becomes

$$\begin{aligned} -\frac{1}{2}\frac{Y(\theta,\phi)}{r}\frac{\partial^2\xi(r)}{\partial r^2} - \frac{\xi(r)}{r^3}\frac{1}{2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) + \frac{1}{r}V(r)\,\xi(r)\,Y(\theta,\phi) \\ = \frac{1}{r}E_H(r)\,\xi(r)\,Y(\theta,\phi) \end{aligned} \tag{2.41}$$

Using the result for the angular part of the problem we derived before, this can be simplified to

$$\frac{-1}{2}\frac{d^2\xi(r)}{dr^2} + \left(V(r) + \frac{1}{2}\frac{l(l+1)}{r^2}\right)\xi(r) = E_H\xi(r) \tag{2.42}$$

where we have written the partial derivatives as total derivatives because the equation has a single independent variable r. The analysis presented here is valid for any potential $V(r)$ that is only dependent on r i.e. for any central potential. Depending on the nature of the function $V(r)$, the form of the actual differential equation and consequently, the wave-function, changes. The nature of the wave function for the electrostatic potential in equation (2.3) is calculated using the following method: We first attempt to isolate the functional forms that are present in the solution wave-function by analysing the behaviour of the differential equation in the limiting cases, i.e when $r \to 0$ and $r \to \infty$. This leaves us with a bunch of known functional components of the solution and an unknown component. We substitute this into the original equation to get a new differential equation for the unknown function. We find this function in the second step by equating it to a polynomial power series and calculate its coefficients. Carrying out such a functional analysis for the radial equation, we find the final result for $\xi(r)$ and hence for $R(r) = \frac{\xi(r)}{r}$

$$R_{nl}(r) = \left[\frac{(n-l-1)!}{2n(n+l)!}\left(\frac{2}{n}\right)^3\right]^{\frac{1}{2}}\left(\frac{2r}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{n}\right)\exp\left(-\frac{r}{n}\right) \tag{2.43}$$

For the solution to have a terminating power series, the condition on the integer n is that

$$n \geq l + 1 \tag{2.44}$$

The Stern-Gerlach experiment shows that electrons have a magnetic moment, which we term as the spin. Electrons are know to have a spin angular momentum of $\sigma = \frac{1}{2}$, so that the spin quantum number can take the values $m_s = \pm\frac{1}{2}$. We do not derive the spin character of the electron in the hydrogen atom from the Schrödinger equation. Hence, we add a spin function to our hydrogenic wave-function independently as function $\varrho(\sigma)$ so that our complete wave function now looks like

$$\varphi_{n,l,m,\sigma}(\mathbf{r}) = R(r)\, Y(\theta,\phi)\, \varrho(\sigma) \tag{2.45}$$

We now have the eigenfunctions that satisfy the Schrödinger equation for the hydrogen atom. We can also now find the eigenenergies of the hydrogen atoms corresponding to the different values of n.

$$E_n = -\frac{1}{2n^2} \tag{2.46}$$

We can also summarise the different quantum numbers and their values from the eigenvalues and eigenfunctions of the Schrödinger equation.

$$\begin{aligned} n &= 1,2,3,\ldots && \text{(principal quantum number)} \\ l &= 0,1,\ldots,(n-1) && \text{(orbital quantum number)} \\ m &= -l,-l+1,\ldots,l-1,l && \text{(magnetic quantum number)} \end{aligned}$$

It is evident that the permitted energy levels for the electron are inversely proportional to the square of the principal quantum number n, and completely independent of the quantum number l and m. Note that for a given value of n, we can have n different values for the quantum number l, and for each l, we can have $2l + 1$ values of m. The spin does not affect the eigenenergies of the hydrogen atom, and the wave-functions corresponding to the two different spin functions are degenerate. Thus we have for a given value of n, $2n^2$ degenerate states.

Another thing to note here is that, although we solved this equation for a hydrogen atom, i.e. a unit nuclear charge, the same procedure is valid for any single electron system with a larger nuclear charge Z. The eigenenergies are scaled by a factor of Z^2.

2.2. Multi-electron atoms

The main difficulty arises when we have atoms with more than one electron in the system. With multi-electron systems, we have an additional term - the electron-electron interaction - appearing in the Hamiltonian. This introduces additional complexity, and the problem is no longer soluble analytically. The idea used in such problems is to replace the instantaneous action of electrons on one another by an averaged action of all electrons on one electron. This method, is of course approximate. A brief discussion of this method follows.

2.2.1. Mean Field Approximation

One of the methods of finding the solutions of the Schrödinger equation for many-electron atoms is the so-called Mean Field Approximation [3]. The Hamiltonian for the system under consideration, neglecting the relativistic and spin-orbit interactions, is given by

$$\hat{\mathcal{H}} = \sum_i \left[-\frac{1}{2}\Delta_i - \frac{Z}{r_i} \right] + \sum_{i<j} \frac{1}{|\vec{r_i} - \vec{r_j}|} \tag{2.47}$$

where Z is the nuclear charge. The first term constitutes the single particle contribution to the Hamiltonian, coming from the kinetic term and the interaction of the electron with the nucleus. The second term is the Coulomb term which comprises of the electrostatic interaction between the electrons. This term is the one that makes the problem "many-body" in character and introduces more complexity into it. We need to solve the Schrödinger equation

$$\hat{\mathcal{H}}\Psi = E\Psi \tag{2.48}$$

for the eigenenergies E and the many-body anti-symmetrised wave-functions Ψ of the system.

First, we observe that the electrostatic interaction coming from the closed shells in an atom is independent of the angular co-ordinates and is spherical in nature. This can be seen from the fact that

$$\sum_{m=-l}^{l} |Y_{lm}(\theta, \phi)|^2 = constant \tag{2.49}$$

In general, the contribution of open shells to the electrostatic potential is not spherically symmetric. In the central field approximation, we enforce spherical symmetry for the potential contributions from the open shells, by spherically averaging this potential. We now use this to split the Hamiltonian into two parts. A term $U_i\left(r_i\right)$ is introduced to contain the average effect of the electrostatic interaction. This term is assumed to be spherical. Then we rewrite the Hamiltonian as

$$\begin{aligned}
\hat{\mathcal{H}} &= \sum_i \left[-\frac{1}{2}\Delta_i - \frac{Z}{r_i}\right] + \sum_{i<j} \frac{1}{|\vec{r_i} - \vec{r_j}|} \\
&= \underbrace{\left(\sum_i \left[-\frac{1}{2}\Delta_i - \frac{Z}{r_i} + U_i\left(r_i\right)\right]\right)}_{\hat{\mathcal{H}}_0} + \underbrace{\left(\sum_{i<j} \frac{1}{|\vec{r_i} - \vec{r_j}|} - \sum_i U_i\left(r_i\right)\right)}_{\hat{\mathcal{H}}_1} \\
&= \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1
\end{aligned} \tag{2.50}$$

Note that $U_i\left(r_i\right)$ is subtracted from $\hat{\mathcal{H}}_1$ to avoid double counting to give an expression that is exactly equivalent to the one in equation (2.47). The radially symmetric part $U_i\left(r_i\right)$ forms a large part of the electron-electron interaction, so $\hat{\mathcal{H}}_1$ is much smaller than $\hat{\mathcal{H}}_0$. Then the problem can be solved by solving the Schrödinger equation for $\hat{\mathcal{H}}_0$ and then treating $\hat{\mathcal{H}}_1$ as a small perturbation.

Now, $\hat{\mathcal{H}}_0$ is centrally symmetric and hence commutes with the angular momentum. The quantum numbers n, l, m_l and m_s still characterise the eigenfunctions, but the degeneracy in l may or may not exist, as the effective potential is not Coulomb-like. The biggest difficulty is indeed finding the exact form of the central potential $U_i\left(r_i\right)$, because it requires the knowledge of the wave-functions of all the other electrons. An iterative approach is needed to solve the Schrödinger equation for each electron, and then to iteratively improve the function $U_i\left(r_i\right)$.

The self-consistent field method can be used to estimate $U_i\left(r_i\right)$. This is based on the variational approach due to Hartree. If the electrons are considered independent, then the total wave-function is a product state of the individual electronic wave-functions. So for an N electron system,

$$\Psi\left(\{\mathbf{r}_\nu\}\right) = \varphi_{\nu_1}\left(\mathbf{r}_1\right)\varphi_{\nu_2}\left(\mathbf{r}_2\right)\ldots\varphi_{\nu_N}\left(\mathbf{r}_N\right) \tag{2.51}$$

where $\nu_i = \left(nlm_lm_s\right)$ is the set of quantum numbers associated with the single-particle wave-function. Now, this wave-function is not actually a antisymmetric Slater determinant. The Pauli principle is preserved by imposing the condition that each set of ν_i is different in at least one quantum number. This product state is used as a trial wave-function and then using the variational principle, the energy $E\left[\Psi\left(\{\mathbf{r}_\nu\}\right)\right] = \langle\Psi|\,\hat{\mathcal{H}}\,|\Psi\rangle$ is minimised. We impose the normalisation using Lagrange parameters ε_i to get the Hartree equations from the energy minimisation

$$\left(-\frac{\nabla^2}{2}-\frac{Z}{r}\right)\varphi_i\left(\mathbf{r}\right)+\sum\int d^3r'\left|\varphi_j\left(\mathbf{r}'\right)\right|^2\frac{1}{\left|\mathbf{r}-\mathbf{r}'\right|}\varphi_i\left(\mathbf{r}\right)=\varepsilon_i\varphi_i\left(\mathbf{r}\right) \tag{2.52}$$

The second term is the term that describes the electrostatic interaction of one electron with the charge densities of the other electrons. This term is then spherically averaged and used as the spherical potential for solving the Schrödinger equation

$$U_i\left(\mathbf{r}_i\right)\mapsto U_i\left(r_i\right)=\int\frac{d\Omega}{4\pi}U_i\left(\mathbf{r}_i\right) \tag{2.53}$$

This method is called the Hartree method. An improved method is called the Hartree Fock method, where the initial guess function is not a simple product state, rather a Slater determinant of the single particle functions.

From these calculations, it becomes evident that although the eigenstates of multi-electron atoms are characterised by the same quantum numbers as for the hydrogen atom - (n, l, m_l, m_s) - the states for a given n and different values of l are not necessarily degenerate. It is observed, that the states with lower l states lying lower in energy. This gives us the Aufbau principle, which helps us identify the ground state configuration of a multi-electron atom.

Usually we are concerned only with the electrons in the outermost shells of the atom, as these are the ones that contribute to chemical reactions and spectra. When the outermost shell has several electrons, the Aufbau principle is often not enough to describe the ground state of the atom. This is because the spins and the orbital angular momenta of the electrons couple in different ways.

2.2.2. Properties of the Central Field Hamiltonian

The Hamiltonian $\hat{\mathcal{H}}$ from equation (2.50) possesses certain properties that are crucial to us for finding its eigenenergies and eigenfunctions [2]. First off, the Hamiltonian describes a system of N particles, which are indistinguishable. This means that the Hamiltonian is invariant under an interchange of particle co-ordinates. Also, it is clear from equation (2.50) that the Hamiltonian is invariant under an inversion $(\mathbf{r}\rightarrow-\mathbf{r})$.

Let $\hat{\mathbf{l}}_i$ denote the angular momentum operator for the i^{th} electron. We define the total angular momentum operator as

$$\hat{\mathbf{L}}=\sum_k^N\hat{\mathbf{l}}_k \tag{2.54}$$

We will discuss the nature of this operator and its associated properties in chapter 3. We can recall from the derivation of the hydrogen atom (2.35) that the the angular momentum operator commutes with the kinetic energy operator in $\hat{\mathcal{H}}_0$. Since the spherically averaged potential $U(r)$ and the electrostatic interaction with the nucleus $\frac{Z}{r_i}$ are just dependent on a scalar variable r, and the angular momentum operator acts only on the angular variables, these terms clearly commute with $\hat{\mathbf{l}}_i$. So, we can conclude that

$$\left[\hat{\mathcal{H}}_0, \hat{\mathbf{L}}\right] = 0 \tag{2.55}$$

Now we turn to the electron-electron interaction part $\hat{\mathcal{H}}_1$. Once again, the spherically averaged correction $U(r_i)$ commutes with $\hat{\mathbf{l}}_i$. Let us now calculate the commutation relation for the Coulomb term with the total angular momentum.

$$\begin{aligned}\left[\sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \hat{\mathbf{L}}\right] &= \left[\sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \sum_k \hat{\mathbf{l}}_k\right] \\ &= \sum_{i<j}\sum_k \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\hat{\mathbf{l}}_k - \sum_{i<j}\sum_k \hat{\mathbf{l}}_k \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\end{aligned} \tag{2.56}$$

Using equation (2.20), $\hat{\mathbf{l}}_k = -i\mathbf{r}_k \times \nabla_k$. We can let the operator act on some arbitrary function Φ,

$$\begin{aligned}\hat{\mathbf{l}}_k\left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\Phi\right) &= \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\hat{\mathbf{l}}_k\Phi + -i\mathbf{r}_k \times \nabla_k \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\Phi \\ \Rightarrow \hat{\mathbf{l}}_k\left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right) &= \left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right)\hat{\mathbf{l}}_k - i\mathbf{r}_k \times \nabla_k\left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right)\end{aligned} \tag{2.57}$$

Substituting this into equation (2.56), we get

$$\begin{aligned}\left[\sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \hat{\mathbf{L}}\right] &= i\sum_{i<j}\sum_k \mathbf{r}_k \times \nabla_k \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &= i\sum_{i<j}\left(\frac{\mathbf{r}_i \times \mathbf{r_j}}{|\mathbf{r}_i - \mathbf{r}_j|^3} + \frac{\mathbf{r}_j \times \mathbf{r}_i}{|\mathbf{r_i} - \mathbf{r}_j|^3}\right) \\ &= 0\end{aligned} \tag{2.58}$$

Therefore we see that $\hat{\mathcal{H}}_1$ also commutes with $\hat{\mathbf{L}}$, which helps us to conclude that

$$\left[\hat{\mathcal{H}}, \hat{\mathbf{L}}\right] = 0 \tag{2.59}$$

Further, we also see that the Hamiltonian $\hat{\mathcal{H}}$ is completely independent of the spins of the electrons. Thus, if we define another operator $\hat{\mathbf{S}} = \sum_k \hat{\mathbf{s}}_k$ where $\hat{\mathbf{s}}_k$ is the spin operator of a single electron, we can see that,

$$\left[\hat{\mathcal{H}}, \hat{\mathbf{S}}\right] = 0 \tag{2.60}$$

Relations 2.59 and 2.60 will help us later in defining a suitable basis for solving the electrostatic Hamiltonian. Before we go into greater details about the electrostatic problem, it will be useful for us to see more terms that can appear in the Hamiltonian, so that we can have a complete understanding of the problem at hand.

2.2.3. Spin-Orbit Coupling

A relativistic correction term needs to be added to the Hamiltonian, especially for higher values of nuclear charge. This term appears due to the coupling between the spin and the orbital degrees of freedom. Qualitatively, the origin of the spin-orbit coupling can be understood as follows. The atomic nucleus creates an electric field through which the electron moves, which is experienced as a magnetic field by the electron in its rest frame. The Hamiltonian will thus contain a term that describes the orientation of the electron spin with respect to this magnetic field. This term can be written as

$$\hat{\mathcal{H}}_2 = \sum_i \xi\left(r_i\right) \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i \tag{2.61}$$

Now we recall from equation (2.58) that the electrostatic Hamiltonian commutes with the $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ operators. This means that it also commutes with $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. It can be shown that with regards to the spin orbit coupling term, although $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ does not commute with either of $\hat{\mathbf{L}}$ or $\hat{\mathbf{S}}$ individually, it does commute with $\hat{\mathbf{J}}$. Depending on the relative strengths of the electrostatic interaction and the spin-orbit coupling, there are two distinct methods in which the angular and spin degrees of freedom of the individual electrons couple.

- Russell-Saunders (LS) Coupling:
  When $\hat{\mathcal{H}}_1 \gg \hat{\mathcal{H}}_2$ we first couple the orbital angular momenta($\hat{\mathbf{L}} = \sum_i \hat{\mathbf{l}}_i$) and spins($\hat{\mathbf{S}} = \sum_i \hat{\mathbf{s}}_i$) separately for all electrons, and then add the total orbital momentum and total spin to calculate $\hat{\mathbf{J}}$.
- jj Coupling:
  When $\hat{\mathcal{H}}_2 \gg \hat{\mathcal{H}}_1$, we choose to couple the angular momentum of individual electrons first $\hat{\mathbf{j}}_i = \hat{\mathbf{l}}_i + \hat{\mathbf{s}}_i$ and then combine the individual $\hat{\mathbf{j}}_i$ to get $\hat{\mathbf{J}} = \sum_i \hat{\mathbf{j}}_i$.

2.2.4. Crystal Fields

All the interactions we spoke of until now are valid in the case of a free atom. But once we talk about atoms in crystalline solids, we need to consider the effects of the neighbouring atoms (or *ligands*) in the crystal. We were assuming a central potential until now, but in a molecule or in a solid, this symmetry is reduced because of the crystal field. In general, there are two different kinds of effects that come out due to the crystal field [6]. One is simply the Coulomb interaction with the ions surrounding the atom. The other one is a transfer of charge from the central atom to the ligand atoms due to the overlap of their wave-functions.

We are only going to look at the Coulomb interaction between the central atom and the ligand. This is a static field, and is called a *crystalline electric field* (CEF). In the model that we use, each ligand is approximated by a point charge, and hence, the crystal is approximated simply by a cage of point charges.

When we consider the transition metals (especially the $3d$ ions), we observe that many compounds exhibit an octahedral or tetrahedral potential due to the surrounding ligands, which are usually non-metal ions. The direct consequence of this is that the the degeneracies of the electrostatic Hamiltonian are lifted, and a splitting of these energy levels takes place. From group theory arguments, it can be deduced whether or not a particular energy level splits. But it does not give any idea about the magnitudes of the split.

CHAPTER 3

Angular Momentum

We briefly introduced the angular momentum operators while discussing the hydrogen atom. Although the treatment was restricted to that system, a general theory of angular momenta exists, which is crucial for us in understanding the theory of multiplets. We will first look at some properties of a generalised angular momentum operator. Since our ultimate goal is to deal with multi-electron atoms, it is obvious that we need to deal with multiple angular momenta together. Another level of complexity arises when we start dealing with the electron spins, as that constitutes an additional angular degree of freedom for the electron. [4]

3.1. General Formalism of Angular Momentum

A general angular momentum $\vec{J}$, that can be defined by its three components $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$, satisfies the following commutation relations in $p, q, r \in \{x, y, z\}$

$$\left[\hat{J}_p, \hat{J}_q\right] = i\varepsilon_{pqr}\hat{J}_r \tag{3.1}$$

where ε_{pqr} is the Levi-Civita symbol. $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ are Hermitian and have real eigenvalues. The individual components do not commute with each other, so they don't have common eigenstates. The square of the angular momentum is a scalar operator. So, it commutes with the individual components of the angular momentum

$$\left[\hat{\mathbf{J}}^2, \hat{J}_k\right] = 0\,;\; k \in \{x, y, z\} \tag{3.2}$$

$\hat{\mathbf{J}}^2$ can be simultaneously diagonalised individually with each component of the angular momentum. As a convention, we choose to find the joint eigenstates of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$. We choose to represent the joint eigenstates as $|\alpha, \beta\rangle$ and then the eigenvalue equations as

$$\begin{aligned} \hat{\mathbf{J}}^2 \left|\alpha, \beta\right\rangle &= \alpha \left|\alpha, \beta\right\rangle \\ \hat{J}_z \left|\alpha, \beta\right\rangle &= \beta \left|\alpha, \beta\right\rangle \end{aligned} \tag{3.3}$$

The eigenstates are orthonormal, and the orthonormality condition is given by

$$\left\langle \alpha, \beta | \alpha', \beta' \right\rangle = \delta_{\alpha\alpha'}\delta_{\beta\beta'} \tag{3.4}$$

We can now introduce raising and lowering operators $\hat{J}_\pm$ associated with $\hat{J}_z$

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \tag{3.5}$$

Then we can express $\hat{J}_x$ and $\hat{J}_y$ in terms of the raising and lowering operators as

$$\hat{J}_x = \frac{1}{2}\left(\hat{J}_+ + \hat{J}_-\right) \quad ; \quad \hat{J}_y = \frac{1}{2i}\left(\hat{J}_+ - \hat{J}_-\right) \tag{3.6}$$

The following commutation relations hold for the raising and lowering operators.

$$\left[\hat{\mathbf{J}}^2, \hat{J}_\pm\right] = 0, \quad \left[\hat{J}_+, \hat{J}_-\right] = 2\hat{J}_z, \quad \left[\hat{J}_z, \hat{J}_\pm\right] = \pm\hat{J}_\pm \tag{3.7}$$

It is useful to note that the following expressions describe the $\hat{\mathbf{J}}^2$ operator in terms of the raising and lowering operators

$$\hat{\mathbf{J}}^2 = \hat{J}_\pm\hat{J}_\mp + \hat{J}_z^2 \mp \hat{J}_z = \frac{1}{2}\left(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+\right) + \hat{J}_z^2 \tag{3.8}$$

Consider

$$\hat{J}_z\left(\hat{J}_\pm\left|\alpha,\beta\right\rangle\right)=\left(\hat{J}_\pm\hat{J}_z\pm\hat{J}_\pm\right)\left|\alpha,\beta\right\rangle=(\beta\pm1)\left(\hat{J}_\pm\left|\alpha,\beta\right\rangle\right) \tag{3.9}$$

which means that $\left(\hat{J}_\pm\left|\alpha,\beta\right\rangle\right)$ is an eigenstate of the $\hat{J}_z$ operator, and then due to the commutation relation (3.7), also an eigenstate of the $\hat{\mathbf{J}}^2$ operator. Now since $\hat{\mathbf{J}}^2$ and $\hat{J}_\pm$ commute, we can write

$$\hat{\mathbf{J}}^2\left(\hat{J}_\pm\left|\alpha,\beta\right\rangle\right)=\hat{J}_\pm\left(\hat{\mathbf{J}}^2\left|\alpha,\beta\right\rangle\right)=\alpha\left(\hat{J}_\pm\left|\alpha,\beta\right\rangle\right) \tag{3.10}$$

Thus we can deduce that the raising and lowering operators leave the $\hat{\mathbf{J}}^2$ eigenvalue unchanged, but increment or decrement the $\hat{J}_z$ eigenvalue by 1. So, we can postulate that

$$\hat{J}_\pm\left|\alpha,\beta\right\rangle=\Gamma^\pm_{\alpha\beta}\left|\alpha,\beta\pm1\right\rangle \tag{3.11}$$

where $\Gamma^\pm_{\alpha\beta}$ is a coefficient of proportionality dependent on α, β and on whether the operator is raising or lowering. Now the matrix elements of $\hat{\mathbf{J}}^2-\hat{J}_z^2=\hat{J}_x^2+\hat{J}_y^2$ are positive which means

$$\left\langle\alpha,\beta\right|\hat{\mathbf{J}}^2-\hat{J}_z^2\left|\alpha,\beta\right\rangle=\alpha-\beta^2\geq0\Rightarrow\alpha\geq\beta^2 \tag{3.12}$$

Thus, β has an upper limit at some β_{max}. This also means that there exists a state that cannot be raised further using the $\hat{J}_+$ operator. Hence,

$$\begin{aligned}
&\hat{J}_+\left|\alpha,\beta_{max}\right\rangle=0\\
\Rightarrow\ &\hat{J}_-\hat{J}_+\left|\alpha,\beta_{max}\right\rangle=0\\
\Rightarrow\ &\left(\hat{\mathbf{J}}^2-\hat{J}_z^2-\hat{J}_z\right)\left|\alpha,\beta_{max}\right\rangle=0\\
\Rightarrow\ &\left(\alpha-\beta_{max}^2-\beta_{max}\right)\left|\alpha,\beta_{max}\right\rangle=0\\
\Rightarrow\ &\alpha=\beta_{max}\left(\beta_{max}+1\right)
\end{aligned} \tag{3.13}$$

Similarly, there is also a lower limit β_{min} on the value of β which can be obtained by a successive application of the lowering operator to the eigenstate $\left|\alpha,\beta_{max}\right\rangle$. The resultant state obeys

$$\hat{J}_{-}\left|\alpha,\beta_{min}\right\rangle = 0 \tag{3.14}$$

Similar to the arguments used in (3.13), we can deduce that

$$\alpha = \beta_{min}\left(\beta_{min} - 1\right) \tag{3.15}$$

From this, we can infer that $\beta_{max} = -\beta_{min}$. Suppose we obtained β_{min} after k successive applications of $\hat{J}_{-}$ to $\left|\alpha,\beta_{max}\right\rangle$,

$$\beta_{max} = \beta_{min} + k \Rightarrow \beta_{max} = -\beta_{min} = \frac{k}{2} \tag{3.16}$$

This means that β can take only integer or half-integer values. Now, we introduce a new notation which will help us relate our analysis of a general angular momentum to the orbital angular momentum discussed previously in chapter 2. Put $\beta_{max} = j$ and $\beta = m$ so that $j = k/2$ and hence

$$\alpha = j\left(j + 1\right) \tag{3.17}$$

and from (3.12),

$$-j \leq m \leq j; \quad m = -j, -j + 1, \ldots, j - 1, j \tag{3.18}$$

Then we can finally summarise our eigenvalue equation in (3.3) as

$$\begin{aligned} \hat{\mathbf{J}}^2\left|j,m\right\rangle &= j\left(j+1\right)\left|j,m\right\rangle \\ \hat{J}_z\left|j,m\right\rangle &= m\left|j,m\right\rangle \end{aligned} \tag{3.19}$$

and then the orthonormality condition for the eigenstates is given by

$$\left\langle j,m|j',m'\right\rangle = \delta_{jj'}\delta_{mm'} \tag{3.20}$$

Now we can derive the value for the coefficients $\Gamma^{\pm}_{\alpha\beta} = \Gamma^{\pm}_{jm}$. Consider

$$\left(\hat{J}_+ \left|j,m\right\rangle\right)^\dagger \left(\hat{J}_+ \left|j,m\right\rangle\right) = \left|\Gamma^+_{jm}\right|^2 \left\langle j,m+1|j,m+1\right\rangle = \left|\Gamma^+_{jm}\right|^2 \tag{3.21}$$

But,

$$\begin{aligned} \left(\hat{J}_+ \left|j,m\right\rangle\right)^\dagger \left(\hat{J}_+ \left|j,m\right\rangle\right) &= \left\langle j,m\right| \hat{J}_- \hat{J}_+ \left|j,m\right\rangle \\ \Rightarrow \left\langle j,m\right| \hat{J}_- \hat{J}_+ \left|j,m\right\rangle &= \left|\Gamma^+_{jm}\right|^2 \end{aligned} \tag{3.22}$$

But since $\hat{J}_- \hat{J}_+ = \hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hat{J}_z$,

$$\begin{aligned} \left|\Gamma^+_{jm}\right|^2 &= \left\langle j,m\right| \hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hat{J}_z \left|j,m\right\rangle \\ \Rightarrow \left|\Gamma^+_{jm}\right|^2 &= j\left(j+1\right) - m^2 - m \\ \Rightarrow \left|\Gamma^+_{jm}\right| &= \sqrt{j\left(j+1\right) - m\left(m+1\right)} \end{aligned} \tag{3.23}$$

Here we have chosen an arbitrary phase, zero, for the constant Γ^+_{jm}. Similarly we can derive Γ^-_{jm}

$$\left|\Gamma^-_{jm}\right| = \sqrt{j\left(j+1\right) - m\left(m-1\right)} \tag{3.24}$$

The relations (3.11) can be simply summarised as

$$\hat{J}_\pm \left|j,m\right\rangle = \sqrt{\left(j \mp m\right)\left(j \pm m + 1\right)} \left|j,m \pm 1\right\rangle \tag{3.25}$$

Using this definition, we can use (3.5) to find the expectation values of the angular momentum components in the x and y directions. It can be shown that

$$\left\langle j,m\right| \hat{J}_x \left|j,m\right\rangle = \left\langle j,m\right| \hat{J}_y \left|j,m\right\rangle = 0 \tag{3.26}$$

3.1.1. Matrix Representation of angular momentum operators

We have already discussed that the set of joint eigenstates of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ - $|j,m\rangle$ forms a complete and orthonormal basis. Thus, in this basis, we can represent all our angular momentum operators as matrices. Using (3.19) and (3.20), we can write that

$$\begin{aligned} \langle j',m'|\,\hat{\mathbf{J}}^2\,|j,m\rangle &= j\,(j+1)\,\delta_{jj'}\delta_{mm'} \\ \langle j',m'|\,\hat{J}_z\,|j,m\rangle &= m\delta_{jj'}\delta_{mm'} \end{aligned} \tag{3.27}$$

Therefore the representative matrices for $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ are diagonal. Further, we can use (3.25) to write the matrix elements for the raising and lowering operators

$$\langle j',m'|\,\hat{J}_\pm\,|j,m\rangle = \sqrt{(j\mp m)\,(j\pm m+1)}\delta_{jj'}\delta_{m\pm 1,m'} \tag{3.28}$$

These matrices are not diagonal. This relation can be used along with (3.6) to write out the matrices for $\hat{J}_x$ and $\hat{J}_x$

$$\begin{aligned} \langle j',m'|\,\hat{J}_x\,|j,m\rangle &= \frac{1}{2}\left(\sqrt{(j-m)\,(j+m+1)}\delta_{m+1,m'} + \sqrt{(j+m)\,(j-m+1)}\delta_{m-1,m'}\right)\delta_{jj'} \\ \langle j',m'|\,\hat{J}_y\,|j,m\rangle &= \frac{1}{2i}\left(\sqrt{(j-m)\,(j+m+1)}\delta_{m+1,m'} - \sqrt{(j+m)\,(j-m+1)}\delta_{m-1,m'}\right)\delta_{jj'} \end{aligned} \tag{3.29}$$

3.2. Addition of two angular momenta

In multi-electron atoms, we need to consider the angular momentum of all the electrons in the atom. One of the many challenges of dealing with the many body problem is to find a suitable basis for representing the many-body Hamiltonian. We have seen in chapter (2) that the total orbital angular momentum and the total spin angular momentum are conserved, and hence, the total orbital angular momentum L, the total spin angular momentum S and the total angular momentum J are good quantum numbers for dealing with the electrostatic interaction in the mean field approximation in the realm of Russell-Saunders Coupling. While we had only mentioned the $\hat{\mathbf{L}}$, $\hat{\mathbf{S}}$ and $\hat{\mathbf{J}}$ in passing before, we will now go into further details on about their evaluation and manipulation.

Let $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ be two angular momenta that belong to two different subspaces 1 and 2. They individually satisfy all the properties of angular momenta we have discussed before. Since they belong to different spaces,

$$\left[\hat{J}_{1i}, \hat{J}_{2j}\right] = 0, \qquad (i, j \in \{x, y, z\}) \tag{3.30}$$

Now we denote the joint eigenstates of $\hat{\mathbf{J}}_1^2$ and $\hat{J}_{1z}$ by $|j_1, m_1\rangle$ and those of $\hat{\mathbf{J}}_2^2$ and $\hat{J}_{2z}$ by $|j_2, m_2\rangle$. Then

$$\begin{aligned}
\hat{\mathbf{J}}_1^2 \left|j_1, m_1\right\rangle &= j_1 \left(j_1 + 1\right) \left|j_1, m_1\right\rangle \\
\hat{J}_{1z} \left|j_1, m_1\right\rangle &= m_1 \left|j_1, m_1\right\rangle \\
\hat{\mathbf{J}}_2^2 \left|j_2, m_2\right\rangle &= j_2 \left(j_2 + 1\right) \left|j_2, m_2\right\rangle \\
\hat{J}_{2z} \left|j_2, m_2\right\rangle &= m_2 \left|j_2, m_2\right\rangle
\end{aligned} \tag{3.31}$$

Now we consider the subspaces 1 and 2 together. The resulting space is a direct product space of 1 and 2, denoted by $1 \otimes 2$ and is of the dimension $(2j_1 + 1)(2j_2 + 1)$. Since the operators $\hat{\mathbf{J}}_1^2$, $\hat{J}_{1z}$, $\hat{\mathbf{J}}_2^2$ and $\hat{J}_{2z}$ are mutually commuting, we can find joint eigenstates for the four operators. The joint eigenstates can be written as the direct products of $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$. We will write them in a combined notation as

$$\left|j_1, m_1; j_2, m_2\right\rangle = \left|j_1, m_1\right\rangle \left|j_2, m_2\right\rangle \tag{3.32}$$

These joint eigenstates form an orthonormal and complete basis in the eigenspace

$$\begin{aligned}
\left\langle j_1, m_1; j_2, m_2 \middle| j_1', m_1'; j_2', m_2' \right\rangle &= \delta_{j_1 j_1'} \delta_{m_1 m_1'} \delta_{j_2 j_2'} \delta_{m_2 m_2'} \\
\sum_{m_1 m_2} \left|j_1, m_1; j_2, m_2\right\rangle \left\langle j_1', m_1'; j_2', m_2'\right| &= \hat{1}
\end{aligned} \tag{3.33}$$

The idea is to generalise the concept of the a single angular momentum to a more general *total angular momentum*, which can be found by adding two different angular momentum operators. Since we already have a formalism for a single angular momentum, we would like the total angular momentum to have similar properties. Intuitively, we can see that the z-component of the total angular momentum and the square of the total angular momentum are two operators that interest us a great deal. Then, we define the total angular momentum operator as

$$\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 \tag{3.34}$$

We want to find the joint eigenstates of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ in terms of the eigenvalues and eigenstates of $\hat{\mathbf{J}}_1^2$, $\hat{J}_{1z}$, $\hat{\mathbf{J}}_2^2$ and $\hat{J}_{2z}$. We can check that the individual components of $\hat{\mathbf{J}}$ satisfy the angular momentum commutation relations, and thus

$$\left[\hat{J}_x, \hat{J}_y\right] = i\hat{J}_z, \quad \left[\hat{J}_y, \hat{J}_z\right] = i\hat{J}_x, \quad \left[\hat{J}_z, \hat{J}_x\right] = i\hat{J}_y \tag{3.35}$$

Another set of operators that commute mutually is $\hat{\mathbf{J}}_1^2$, $\hat{\mathbf{J}}_2^2$, $\hat{\mathbf{J}}^2$ and $\hat{J}_z$. Thus it is also possible to diagonalise these four simultaneously. Let us denote these eigenstates as $|j_1; j_2; j, m\rangle$. Then

$$\begin{aligned}
\hat{\mathbf{J}}_1^2 \left|j_1; j_2; j, m\right\rangle &= j_1 \left(j_1 + 1\right) \left|j_1; j_2; j, m\right\rangle \\
\hat{\mathbf{J}}_2^2 \left|j_1; j_2; j, m\right\rangle &= j_2 \left(j_2 + 1\right) \left|j_1; j_2; j, m\right\rangle \\
\hat{\mathbf{J}}^2 \left|j_1; j_2; j, m\right\rangle &= j \left(j + 1\right) \left|j_1; j_2; j, m\right\rangle \\
\hat{\mathbf{J}}_z \left|j_1; j_2; j, m\right\rangle &= m \left|j_1; j_2; j, m\right\rangle
\end{aligned} \tag{3.36}$$

We can build a transformation from one basis to the other using the identity operator (3.33) as

$$\begin{aligned}
\left|j_1; j_2; j, m\right\rangle &= \left(\sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} \left|j_1, m_1; j_2, m_2\right\rangle \left\langle j_1, m_1; j_2, m_2\right|\right) \left|j_1; j_2; j, m\right\rangle \\
&= \sum_{m_1 m_2} \left\langle j_1, m_1; j_2, m_2 | j_1; j_2; j, m\right\rangle \left|j_1, m_1; j_2, m_2\right\rangle
\end{aligned} \tag{3.37}$$

The matrix elements $\langle j_1, m_1; j_2, m_2 | j_1; j_2; j, m\rangle$ are called Clebsch-Gordan coefficients. They are real by convention. They possess certain properties

$$\sum_{m_1 m_2} \left|\left\langle j_1, m_1; j_2, m_2 | j_1; j_2; j, m\right\rangle\right|^2 = \sum_{j} \sum_{m=-j}^{j} \left|\left\langle j_1, m_1; j_2, m_2 | j_1; j_2; j, m\right\rangle\right|^2 = 1 \tag{3.38}$$

We can find the eigenvalues of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ in terms of j_1, j_2, m_1 and m_2. Since $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$, we can deduce that $m = m_1 + m_2$. Now, as $m_{max} = m_{1max} + m_{2max} = j_1 + j_2$ and $|m| \leq j$, we have that $j_{max} = j_1 + j_2$. Further, the number of eigenstates is equal to the dimension of the product space $(2j_1 + 1)(2j_2 + 1)$. Since each value of j corresponds to $(2j + 1)$ eigenstates,

$$\begin{aligned}\sum_{j=j_{min}}^{j_{max}} (2j+1) &= (2j_1+1)(2j_2+1) \\ \frac{(j_{max}-j_{min}+1)(j_{max}+j_{min})}{2} &= (2j_1+1)(2j_2+1) \qquad (3.39)\end{aligned}$$

This can be simplified to give that $j_{min} = |j_1 - j_2|$ which implies that $|j_1 - j_2| \leq j \leq (j_1 + j_2)$. We can further define certain rules for the Clebsch-Gordan coefficients using these eigenvalues. These coefficients are only non-zero when $m = m_1 + m_2$ and $|j_1 - j_2| \leq j \leq (j_1 + j_2)$.

We can come up with a recursion relation for calculating the Clebsch-Gordan coefficients. The limiting cases where $m_1 = j_1$, $m_2 = j_2$, $j = j_1 + j_2$, $m = j_1 + j_2$ and $m_1 = -j_1$, $m_2 = -j_2$, $j = j_1 + j_2$, $m = -(j_1 + j_2)$ are easy to calculate from (3.37) since the corresponding expressions have only one term on the right hand side.

$$\langle j_1, j_1; j_2, j_2 | j_1; j_2; (j_1+j_2), (j_1+j_2)\rangle = \langle j_1, -j_1; j_2, -j_2 | j_1; j_2; (j_1+j_2), -(j_1+j_2)\rangle = 1 \qquad (3.40)$$

This expression is valid only up to a phase, depending on the convention being used.

The idea behind formulating the recursion relationship is to calculate the matrix elements $\langle j_1, m_1; j_2, m_2| \hat{J}_\pm |j_1; j_2; j, m\rangle$ in two different ways, once applying the operators to the bra and then to the ket. In both methods, we calculate the same value. So, recalling that $\left(\hat{J}_\pm\right)^\dagger = \hat{J}_\mp$,

$$\langle j_1, m_1; j_2, m_2| \left(\hat{J}_\pm |j_1; j_2; j, m\rangle\right) = \left(\hat{J}_\mp |j_1, m_1; j_2, m_2\rangle\right) |j_1; j_2; j, m\rangle \qquad (3.41)$$

$$\begin{aligned}\sqrt{(j \mp m)(j \pm m + 1)}\, \langle j_1, m_1; j_2, m_2 | j_1; j_2; j, m \pm 1\rangle = \\ \sqrt{(j_1 \pm m_1)(j_1 \mp m_1 + 1)}\, \langle j_1, m_1 \mp 1; j_2, m_2 | j_1; j_2; j, m\rangle \\ + \sqrt{(j_2 \pm m_2)(j_2 \mp m_2 + 1)}\, \langle j_1, m_1; j_2, m_2 \mp 1 | j_1; j_2; j, m\rangle \qquad (3.42)\end{aligned}$$

This relationship along with (3.42) can be used to calculate all the Clebsch-Gordan coefficients.

CHAPTER 4

Electrostatic Problem

4.1. Creation and Annihilation Operators

We will now define the fermionic creation and annihilation operators which we will use to define all the angular momentum and operators for interactions that appear later [1]. The way we approach these is by first recalling the nature of any many-body fermionic wave function. For the case of identical fermions, each fermion occupies one of the many single particle states. In general, the number of available single particle states need not be equal to the number of particles. Suppose we have n single particle states, each state denoted by its own set of quantum numbers $a, b, c, \ldots, n$. We assume that these single particle states are orthonormalised. Since we are dealing with fermions, each single particle state can either be occupied by a single particle, or be empty. Let us say we have N particles, which occupy the n states. The many-body wave function will be the Slater determinant of the single particle states.

$$|\Psi_{N;a,b,\ldots,n}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |1,a\rangle & |2,a\rangle & \cdots & |N,a\rangle \\ |1,b\rangle & |2,b\rangle & \cdots & |N,b\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |1,n\rangle & |2,n\rangle & \cdots & |N,n\rangle \end{vmatrix} \tag{4.1}$$

Here we assume that all the n single-particle states are occupied. This is, however, not necessary. In general, each single-particle state can either be occupied or be empty. This can be made clearer using a concrete example. Consider a system of three particles. We again label the available single particle states as $a, b, \ldots, n$. Suppose that the three particles occupy the states a, d and k, while the rest of the states are unoccupied. It is important to use a consistent method of ordering the single particle states in this notation, as the sign of the determinant will change upon reordering the single particle states. We will now order all the states in alphabetical order and call this the standard ordering. At this point we can introduce the occupation number notation, which explicitly denotes the occupations of the individual single particle states.

$$\begin{aligned} |\Psi_{3;a,d,k}\rangle &= \frac{1}{\sqrt{3!}} \begin{vmatrix} |1,a\rangle & |2,a\rangle & |3,a\rangle \\ |1,d\rangle & |2,d\rangle & |3,d\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \end{vmatrix} \\ &= |1_a, 0_b, \ldots, 1_d, 0_e, \ldots, 0_j, 1_k, \ldots\rangle \end{aligned} \tag{4.2}$$

Here 0_b denotes that the single particle state b is unoccupied whereas 1_a means that the single particle state a is occupied.

We posit, now, the existence of a fermionic creation operator for a single particle state. The fermionic creation operator $c_j^\dagger$ converts a many-body state in which the single particle state ϕ_j is empty into a many-body state where ϕ_j is occupied. In determinant notation, ignoring the pre-factors for a moment,

$$c_j^\dagger \begin{vmatrix} |1,a\rangle & |2,a\rangle & |3,a\rangle \\ |1,d\rangle & |2,d\rangle & |3,d\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \end{vmatrix} = \begin{vmatrix} |1,a\rangle & |2,a\rangle & |3,a\rangle & |4,a\rangle \\ |1,d\rangle & |2,d\rangle & |3,d\rangle & |4,d\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \end{vmatrix} \tag{4.3}$$

The fermionic creation operator adds a new particle to the single particle state j. This corresponds to an additional row at the bottom and an additional column to the right of the Slater determinant. Now this determinant is not, in general, in standard order. To make the wave function standard ordered, we need to swap the two rows at the bottom of the Slater determinant, which flips the sign of the determinant.

$$c_j^\dagger \begin{vmatrix} |1,a\rangle & |2,a\rangle & |3,a\rangle \\ |1,d\rangle & |2,d\rangle & |3,d\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \end{vmatrix} = - \begin{vmatrix} |1,a\rangle & |2,a\rangle & |3,a\rangle & |4,a\rangle \\ |1,d\rangle & |2,d\rangle & |3,d\rangle & |4,d\rangle \\ |1,j\rangle & |2,j\rangle & |3,j\rangle & |4,j\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \end{vmatrix} \tag{4.4}$$

In general, the sign of the wave-function depends on the number of row swaps $\mathcal{S}_j$ required to get the determinant in standard order. This can be formalised using the occupation number notation, which we will eventually use extensively

$$c_j^\dagger \left|\ldots, 0_j, \ldots\right\rangle = (-1)^{\mathcal{S}_j} \left|\ldots, 1_j, \ldots\right\rangle \tag{4.5}$$

Along these lines we define the fermionic annihilation operator. Using equation (4.5),

$$\left\langle \ldots, 1_j, \ldots\right| c_j^\dagger \left|\ldots, 0_j, \ldots\right\rangle = (-1)^{\mathcal{S}_j} \tag{4.6}$$

Taking the Hermitian adjoint on both sides

$$\begin{aligned}\Big(\left\langle \ldots, 1_j, \ldots\right| c_j^\dagger \left|\ldots, 0_j, \ldots\right\rangle\Big)^\dagger &= \Big(c_j^\dagger \left|\ldots, 0_j, \ldots\right\rangle\Big)^\dagger \left(\left\langle \ldots, 1_j, \ldots\right|\right)^\dagger \\ &= \left\langle \ldots, 0_j, \ldots\right| c_j \left|\ldots, 1_j, \ldots\right\rangle \\ &= (-1)^{\mathcal{S}_j}\end{aligned} \tag{4.7}$$

Thus,

$$c_j \left|\ldots, 1_j, \ldots\right\rangle = (-1)^{\mathcal{S}_j} \left|\ldots, 0_j, \ldots\right\rangle \tag{4.8}$$

Thus, the operator c_j converts a many-body state in which the single particle state j is occupied, into a many-body state where the state j is empty. We call c_j the fermionic annihilation operator. It can be shown that the creation and annihilation operators obey the following anti-commutation relationships

$$\begin{aligned}\left\{c_i^\dagger, c_j^\dagger\right\} = \{c_i, c_j\} &= 0 \\ \left\{c_i^\dagger, c_j\right\} &= \delta_{ij}\end{aligned} \tag{4.9}$$

What happens if we apply a creation operator $c_k^\dagger$ to a many-body state where the single particle state k is already occupied, for example, the many-body state in (4.2) ? The action of the operators adds a new row and a new column to the Slater determinant

$$c_k^\dagger \begin{vmatrix} |1,a\rangle & |2,a\rangle & |3,a\rangle \\ |1,d\rangle & |2,d\rangle & |3,d\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle \end{vmatrix} = - \begin{vmatrix} |1,a\rangle & |2,a\rangle & |3,a\rangle & |4,a\rangle \\ |1,d\rangle & |2,d\rangle & |3,d\rangle & |4,d\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \\ |1,k\rangle & |2,k\rangle & |3,k\rangle & |4,k\rangle \end{vmatrix} \tag{4.10}$$

But we note that now, there are two identical rows in this Slater determinant, which means that the determinant is singular. Thus we can define this action as

$$c_j^\dagger \left|\ldots, 1_j, \ldots\right\rangle = 0 \tag{4.11}$$

Similarly, if we apply the annihilation operator c_j to a many-body state where the single particle state j is empty,

$$c_j \left|\ldots, 0_j, \ldots\right\rangle = 0 \tag{4.12}$$

4.2. U-Matrix in the basis of spherical harmonics

Recall from chapter 2, that we defined the electrostatic part Hamiltonian as

$$\hat{H}_{ES} = \frac{1}{2} \sum_{i \neq j} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} \tag{4.13}$$

We would now like to represent $\hat{H}_{ES}$ in terms of our creation and annihilation operators. We now label this Hamiltonian as $\hat{U}$ which is then defined as

$$\hat{U} = \frac{1}{2} \sum_{i \neq j} U_{\alpha\beta\gamma\delta} c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma \tag{4.14}$$

where we define the coefficient $U_{\alpha\beta\gamma\delta}$ as

$$U_{\alpha\beta\gamma\delta} = \int d\mathbf{r}_1 d\mathbf{r}_2 \overline{\psi_\alpha} \left(\mathbf{r}_1\right) \overline{\psi_\beta} \left(\mathbf{r}_2\right) \frac{1}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|} \psi_\gamma \left(\mathbf{r}_1\right) \psi_\delta \left(\mathbf{r}_2\right) \tag{4.15}$$

The Coulomb repulsion term only depends on the relative distance between the electrons, and is completely independent of the electron spins. This means that we can separate the spatial and spin degrees of freedom in the electron wave-functions. So

$$\psi_\alpha \left(\mathbf{r}_1\right) = \varphi_{\nu_1} \left(\mathbf{r}_1\right) \chi_{\sigma_1} \left(1\right) \tag{4.16}$$

Using this separation, we can rewrite the integral in (4.15) and the spin functions can then be pulled out of the integral.

$$\begin{aligned} U_{\alpha\beta\gamma\delta} &= \langle\alpha\beta|\, \hat{U}\, |\gamma\delta\rangle \\ &= \langle\chi_{\sigma_1}(1)\,\chi_{\sigma_2}(2)\,|\chi_{\sigma_3}(1)\,\chi_{\sigma_4}(2)\rangle \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_{\nu_1}(\mathbf{r}_1)\,\varphi_{\nu_2}(\mathbf{r}_2)\,\frac{1}{r}\varphi_{\nu_3}(\mathbf{r}_1)\,\varphi_{\nu_4}(\mathbf{r}_2) \\ &= U_{\nu_1\nu_2\nu_3\nu_4}\delta_{\sigma_1\sigma_3}\delta_{\sigma_2\sigma_4} \end{aligned} \tag{4.17}$$

Now since the problem relates to a many-electron system of an atom, the function ϕ_ν is hydrogen-like (chapter 2)

$$\varphi_\nu = \varphi_{nlm} = R_{nl}(r)\,Y_l^m(\theta,\phi) \tag{4.18}$$

For finding the U-matrix elements, we expand the r^{-1} term in the integrals, in terms of the spherical harmonics $Y_k^\mu(\theta,\phi)$

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \frac{4\pi}{2k+1} \sum_{\mu=-k}^{k} \overline{Y_k^\mu}(\theta_1,\phi_1)\,Y_k^\mu(\theta_2,\phi_2) \tag{4.19}$$

where $r_<$ is the smaller of r_1 and r_2, and $r_>$ is the larger of r_1 and r_2. Then we can expand the integral in (4.17) into parts: a radial term

$$\begin{aligned} S^{(k)}(n_1l_1,n_2l_2,n_3l_3,n_4l_4) &= \int\int r_1^2dr_1r_2^2dr_2R_{n_1l_1}(r_1)\,R_{n_2l_2}(r_2)\,\frac{r_<^k}{r_>^{k+1}}R_{n_3l_3}(r_1)\,R_{n_4l_4}(r_2) \\ &= \langle R_{n_1l_1}R_{n_2l_2}|\,\frac{r_<^k}{r_>^{k+1}}\,|R_{n_3l_3}R_{n_4l_4}\rangle \end{aligned} \tag{4.20}$$

and two angular terms

$$\begin{aligned} &\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \overline{Y_{l_2}^{m_2}}(\theta_2,\phi_2)\,Y_k^\mu(\theta_2,\phi_2)\,Y_{l_4}^{m_4}(\theta_2,\phi_2) = \langle l_2m_2|k\mu\times l_4m_4\rangle \\ &\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \overline{Y_{l_1}^{m_1}}(\theta_1,\phi_1)\,\overline{Y_k^\mu}(\theta_1,\phi_1)\,Y_{l_3}^{m_3}(\theta_1,\phi_1) = \langle l_1m_1\times k\mu|l_3m_3\rangle \end{aligned} \tag{4.21}$$

Together, we can write $U_{\nu_1\nu_2\nu_3\nu_4}$ as

$$U_{\nu_1\nu_2\nu_3\nu_4} = \sum_{k=0}^{\infty} S^{(k)}\left(n_1l_1, n_2l_2, n_3l_3, n_4l_4\right)\left[\frac{4\pi}{2k+1}\sum_{\mu=-k}^{k}\langle l_1m_1|k\mu \times l_3m_3\rangle\langle l_2m_2 \times k\mu|l_4m_4\rangle\right] \tag{4.22}$$

There is a special notation for the diagonal matrix elements: the direct term

$$\begin{aligned} U_{\nu\nu'} &= U_{\nu\nu'\nu\nu'} \\ &= \sum_{k=0}^{\infty} S^{(k)}\left(nl, n'l', nl, n'l'\right)\left[\frac{4\pi}{2k+1}\sum_{\mu=-k}^{k}\langle lm|k\mu \times lm\rangle\left\langle l'm' \times k\mu|l'm'\right\rangle\right] \\ &= \sum_{k=0}^{\infty} F^{(k)}\left(nl; n'l'\right) a^{(k)}\left(lm; l'm'\right) \end{aligned} \tag{4.23}$$

and the exchange term

$$\begin{aligned} J_{\nu\nu'} &= U_{\nu\nu'\nu'\nu} \\ &= \sum_{k=0}^{\infty} S^{(k)}\left(nl, n'l', n'l', nl\right)\left[\frac{4\pi}{2k+1}\sum_{\mu=-k}^{k}\left\langle lm|k\mu \times l'm'\right\rangle\left\langle l'm' \times k\mu|lm\right\rangle\right] \\ &= \sum_{k=0}^{\infty} G^{(k)}\left(nl; n'l'\right) b^{(k)}\left(lm; l'm'\right) \end{aligned} \tag{4.24}$$

These radial integrals $F^{(k)}\left(nl; n'l'\right)$ and $G^{(k)}\left(nl; n'l'\right)$ are also called Slater integrals.

In the case of our problem of open shell electrons, all the electrons have the same n and l quantum numbers, in which case, it is easy to see that

$$F^{(k)}\left(nl; nl\right) = G^{(k)}\left(nl; nl\right) \tag{4.25}$$

Then 4.22 will now look like

$$U_{m_1m_2m_3m_4} = \sum_{k=0}^{\infty} F^{(k)}\left(nl; nl\right)\left[\frac{4\pi}{2k+1}\sum_{\mu=-k}^{k}\langle lm_1|k\mu \times lm_3\rangle\langle lm_2 \times k\mu|lm_4\rangle\right] \tag{4.26}$$

Note that now we have explicit dependence on m_1, m_2, m_3 and m_4. We can modify our notation for the diagonal matrix elements so that

$$\begin{aligned} U_{\nu\nu'} = U_{mm'} &= \sum_{k=0}^{\infty} F^{(k)}\left(nl;nl\right) a^{(k)}\left(lm;lm'\right) \\ J_{\nu\nu'} = J_{mm'} &= \sum_{k=0}^{\infty} F^{(k)}\left(nl;nl\right) b^{(k)}\left(lm;lm'\right) \end{aligned} \tag{4.27}$$

For the diagonal matrices, the integrals $a^{(k)}\left(lm;lm'\right)$ are given in Appendix C. For calculations related to electronic structure, it is more useful to have these integrals in the basis of cubic harmonics rather than spherical harmonics. These are also found in Appendix C

4.3. Gaunt coefficients

We will now calculate the angular terms in (4.21). These integrals are called Gaunt coefficients.

$$g^{(l,k)}_{m,m'} = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \overline{Y_l^m}\left(\theta_1,\phi_1\right) Y_k^{\mu}\left(\theta_1,\phi_1\right) Y_{l'}^{m'}\left(\theta_1,\phi_1\right) \tag{4.28}$$

Here, we will use the phase convention due to Condon and Shortley [5]. According to this choice, a factor of -1 appears for spherical harmonics with an odd positive value of m.

$$Y_{lm}\left(\theta,\phi\right) = \left(-1\right)^m \sqrt{\frac{2l+1}{4\pi}\frac{\left(l-m\right)!}{\left(l+m\right)!}} P_l^m\left(\cos\theta\right) \exp\left(im\phi\right) \tag{4.29}$$

where the Legendre Polynomials $P_l^m\left(x\right)$ are given by equation 2.33. Now if we express this integral in terms of the associated Legendre polynomials, we get

$$\begin{aligned} g^{(l,k)}_{m,m'} =& \sqrt{\frac{\left(2l+1\right)\left(2k+1\right)\left(2l+1\right)}{\left(4\pi\right)^3}} \sqrt{\frac{\left(l-m\right)!\left(k-\mu\right)!\left(l-m\right)!}{\left(l+m\right)!\left(k+\mu\right)!\left(l+m\right)}} \times \\ & \int_0^{2\pi} d\phi e^{i\phi\left(-m+\mu+m'\right)} \int_0^{\pi} \sin\theta d\theta P_l^m\left(\cos\theta\right) P_k^{\mu}\left(\cos\theta\right) P_l^{m'}\left(\cos\theta\right) \end{aligned} \tag{4.30}$$

Notice that we do not mention an explicit dependence on μ although we have a spherical harmonic dependent on μ in the integral. From the formula in equation (4.30), we see that the co-efficient $g^{(l,k)}_{m,m'}$ is non-zero only if

$$m - m' = \mu \tag{4.31}$$

Thus m and m' fix the value of μ and we get no explicit dependence on μ. Consequently, we can deduce from equation (4.30) that the Gaunt coefficients will be real, as every non-zero term will have a real exponential term in the ϕ integral. We can then describe our Gaunt coefficients as a two-dimensional matrix in terms of the indices m and m'.

We can of course calculate the Gaunt coefficients using the equation (4.30) above, as all the integrals are known. But this calculation is computationally intensive and is very complicated when represented in code. But we can use another clever way to simplify the calculation. Recall from chapter 3, that the functions $|l,m\rangle$ are eigenfunctions of the angular momentum operator and that they have associated raising and lowering operators.

$$\begin{aligned}\hat{L}_+ |l,m\rangle &= \sqrt{(l-m)(l+m+1)}\,|l,m+1\rangle = \Gamma^+_{lm}|l,m+1\rangle \\ \hat{L}_- |l,m\rangle &= \sqrt{(l+m)(l-m+1)}\,|l,m-1\rangle = \Gamma^-_{lm}|l,m-1\rangle\end{aligned} \tag{4.32}$$

Consider the integral $\left\langle l,m|\hat{L}_+ k,\mu\times l,m'\right\rangle$. We will calculate this integral in two different ways to come up with a recurrence relation between the Gaunt coefficients. First, we can see that the $\hat{L}_\pm$ acts as a differential operator. So we can apply it on the right and use the product rule of differentiation to get

$$\left\langle l,m|\hat{L}_+ k,\mu\times l,m'\right\rangle = \Gamma^+_{k\mu}\langle l,m|k,\mu+1\times l,m'\rangle + \Gamma^+_{lm'}\langle l,m|k,\mu\times l,m'+1\rangle \tag{4.33}$$

But we can also apply the $\hat{L}_+$ to the bra- to get

$$\begin{aligned}\left\langle l,m|\hat{L}_+ k,\mu\times l,m'\right\rangle &= \left(\left(\hat{L}_+\right)^\dagger |l,m\rangle\right)^\dagger |k,\mu\times l,m'\rangle \\ &= \Gamma^-_{lm}\langle l,m-1|k,\mu+1\times l,m'\rangle\end{aligned} \tag{4.34}$$

From the two equations, we can write the relation

$$\Gamma^+_{k\mu}\langle l,m|k,\mu+1\times l,m'\rangle + \Gamma^+_{lm'}\langle l,m|k,\mu\times l,m'+1\rangle = \Gamma^-_{lm}\langle l,m-1|k,\mu\times l,m'\rangle \tag{4.35}$$

We call this relation the $\hat{L}_+$ equation. Similarly, we can also come up with another recurrence relation, the $\hat{L}_-$ equation, using the $\hat{L}_-$ operator

$$\Gamma^-_{k\mu}\left\langle l,m|k,\mu-1\times l,m'\right\rangle + \Gamma^-_{lm'}\left\langle l,m|k,\mu\times l,m'-1\right\rangle = \Gamma^+_{lm}\left\langle l,m+1|k,\mu\times l,m'\right\rangle \tag{4.36}$$

Additionally, the Gaunt coefficient matrix also has certain symmetry properties. First, there is a diagonal symmetry

$$\begin{aligned}
g^{(l,k)}_{m,m'} &= \int d\Omega\, \overline{Y^m_l}\,(\Omega)\, Y^{m-m'}_k\,(\Omega)\, Y^{m'}_l\,(\Omega) \qquad (\,\Omega = (\theta,\phi)\,) \\
&= \overline{\int d\Omega\, \overline{Y^m_l}\,(\Omega)\, Y^{m-m'}_k\,(\Omega)\, Y^{m'}_l\,(\Omega)} \\
&= (-1)^{m-m'} \cdot \int d\Omega\, \overline{Y^{m'}_l}\,(\Omega)\, Y^{m-m'}_k\,(\Omega)\, Y^{m}_l\,(\Omega) \\
&= (-1)^{m-m'} \cdot g^{(l,k)}_{m',m}
\end{aligned} \tag{4.37}$$

There is also anti-diagonal symmetry.

$$\begin{aligned}
g^{(l,k)}_{m,m'} &= \int d\Omega\, \overline{Y^m_l}\,(\Omega)\, Y^{m-m'}_k\,(\Omega)\, Y^{m'}_l\,(\Omega) \qquad (\,\Omega = (\theta,\phi)\,) \\
&= \int d\Omega\, (-1)^m\, Y^{\overline{m}}_l\,(\Omega)\, Y^{m-m'}_k\,(\Omega)\, (-1)^{m'}\, \overline{Y^{\overline{m'}}_l}\,(\Omega) \\
&= (-1)^{m-m'} \cdot \int d\Omega\, \overline{Y^{\overline{m'}}_l}\,(\Omega)\, Y^{m-m'}_k\,(\Omega)\, Y^{\overline{m}}_l\,(\Omega) \\
&= (-1)^{m-m'}\, g^{(l,k)}_{\overline{m'},\overline{m}}
\end{aligned} \tag{4.38}$$

where we are now using the notation $\overline{m} = -m$. The central element in the Gaunt coefficient matrix is easy to calculate because for this element, we have $m = m' = \mu = 0$. Using these central elements, the symmetry properties and the $\hat{L}_+$ and $\hat{L}_-$ equations, we can come up with an algorithm to calculate the Gaunt coefficient matrices for different values of (l, k)

```
void Gaunt( int l_no, int ik, double **gaunt_coeff_matrix )
{
  Initialise_Centre_Element( gaunt_centre_element );

  int iml1 = l_no, iml2 = l_no;

  // Centre element
    gaunt_coeff_matrix[iml1][iml2] = gaunt_centre_element[l_no][ik];

  // First find all the diagonal elements in the +,- direction
  while ( iml2 < ( 2 * l_no ) ) {

    // Find the two elements on either side of the antidiagonal using L_+ equation
```

```
  if ( fabs( Cg_Minus( l_no, iml1-l_no ) + Cg_Plus( l_no, iml2-l_no ) ) < EPSILON ) {
    gaunt_coeff_matrix[iml1-1][iml2] = 0;
    gaunt_coeff_matrix[iml1][iml2+1] = - gaunt_coeff_matrix[iml1-1][iml2];
  } else {
    gaunt_coeff_matrix[iml1-1][iml2] = Cg_Plus( ik, iml1-iml2-1 ) * gaunt_coeff_matrix[iml1][iml2] / ( Cg_Minus( l_no, iml1-l_no ) + Cg_Plus( l_no, iml2-l_no ) );
    gaunt_coeff_matrix[iml1][iml2+1] = - gaunt_coeff_matrix[iml1-1][iml2];
  }

  iml1--;
  iml2++;

  // Use L_- equation to find diagonal element
  if ( fabs( Cg_Minus( ik, iml1-iml2+1 ) ) < EPSILON ) {
    gaunt_coeff_matrix[iml1][iml2] = 0;
  } else {
    gaunt_coeff_matrix[iml1][iml2] = ( Cg_Plus( l_no, iml1-l_no ) * gaunt_coeff_matrix[iml1+1][iml2] - Cg_Minus( l_no, iml2-l_no ) * gaunt_coeff_matrix[iml1][iml2-1] )/ Cg_Minus( ik, iml1-iml2+1 );
  } }

// Now use the L_- equation to find the remaining unknowns in the top triangle
for ( iml2 = ( 2 * l_no-1 ); iml2 >= l_no; iml2-- ) {
  for ( iml1 = ( 2 * l_no - 1 - iml2 ); iml1 >= 0; iml1-- ) {
    gaunt_coeff_matrix[iml1][iml2-1] = ( Cg_Plus( l_no, iml1-l_no ) * gaunt_coeff_matrix[iml1+1][iml2] - Cg_Minus( ik, iml1-iml2+1 ) * gaunt_coeff_matrix[iml1][iml2] )/ Cg_Minus( l_no, iml2-l_no );
  } }

for ( iml2 = ( l_no - 1 ); iml2 >= 1; iml2-- ) {
  for ( iml1 = iml2 - 1; iml1 >= 0; iml1-- ) {
    gaunt_coeff_matrix[iml1][iml2-1] = ( Cg_Plus( l_no, iml1-l_no ) * gaunt_coeff_matrix[iml1+1][iml2] - Cg_Minus( ik, iml1-iml2+1 ) * gaunt_coeff_matrix[iml1][iml2] )/ Cg_Minus( l_no, iml2-l_no );
  } }

// Now the north triangle is filled. Now to mirror these guys about
// the diagonal and antidiagonal.
// First find the east triangle by using antidiagonal symmetry.
for ( iml1 = 1; iml1 <= l_no; iml1++ ) {
  for ( iml2 = ( 2 * l_no ); iml2 >= ( 2 * l_no + 1 - iml1 ); iml2-- ) {
    int temp_sign = 1;
    for ( int ii = 0; ii < fabs( iml1 - iml2 ); ii++ ) {
      temp_sign=-temp_sign;  }
    gaunt_coeff_matrix[iml1][iml2] = temp_sign*gaunt_coeff_matrix[2*l_no-iml2][2*l_no-iml1];
  } }

for ( iml1 = ( l_no + 1 ); iml1 <= ( 2 * l_no ); iml1++ ) {
  for ( iml2 = ( iml1 ); iml2 <= ( 2 * l_no ); iml2++ ) {
    int temp_sign = 1;
    for ( int ii = 0; ii < fabs( iml1 - iml2 ); ii++ ) {
      temp_sign=-temp_sign;  }
```

```
      gaunt_coeff_matrix[iml1][iml2] = temp_sign*gaunt_coeff_matrix[2*l_no-iml2][2*l_no-iml1];
    } }

  // Now find the south and the west triangles using diagonal symmetry
  for ( iml1 = 1; iml1 <= ( 2 * l_no ); iml1++ ) {
    for ( iml2 = 0; iml2 <= ( iml1 - 1 ); iml2++ ) {
      int temp_sign = 1;
      for ( int ii = 0; ii < fabs( iml1 - iml2 ); ii++ ) {
        temp_sign=-temp_sign; }
      gaunt_coeff_matrix[iml1][iml2] = temp_sign*gaunt_coeff_matrix[iml2][iml1];
} } }
```

Listing 4.1: Calculation of Gaunt Coefficients

The Gaunt Co-efficient matrices are listed in Appendix B.

CHAPTER 5

Implementation

5.1. Basis Setup

We work in the basis of occupation numbers [8]. We formally define these basis states using the fermionic creation and annihilation operators. The creation operator $c^\dagger_{n,l,m,\sigma}$ creates an electron with z-component of spin σ in the orbital with principal quantum number n, orbital angular momentum l and z-component of angular momentum m. As a shorthand notation, the quantum numbers (n, l, m, σ) can be denoted by the symbol ν. Analogously, the operator $c_{n,l,m,\sigma}$ annihilates an electron from this spin-orbital. Thus for a system with N electrons, we can write a general many body state as

$$|\Psi\rangle = c^\dagger_{\nu_1} c^\dagger_{\nu_2} \dots c^\dagger_{\nu_N} |0\rangle \tag{5.1}$$

For our problem of interest, we work within a single shell, which means that the n and the l quantum numbers are the same for all electrons. We can shorten the notation by dropping the n and l so that $\nu \equiv (m, \sigma)$. For a given n and l, the following holds for the remaining quantum numbers:

$$\begin{aligned} m &: \ -l \leq m \leq +l \\ \sigma &: \quad \sigma = \pm\frac{1}{2} \end{aligned}$$

Thus, for a fixed shell, we can have $2\,(2l+1)$ possible spin-orbitals to put an electron in. For a system with N electrons, the Hilbert space spans all the distributions of N electrons into $2\,(2l+1)$ spin-orbitals. Using this fact, we can calculate the dimension of the Hilbert space

$$D = \binom{2\,(2l+1)}{N} \tag{5.2}$$

Consequently, we can define a basis on this Hilbert space using the individual distributions. These can be viewed graphically. For example, in the case of a d^4-shell ($l = 2$, $N = 4$), we have 10 sub-orbitals to place the 4 electrons in. One distribution can be written as below

σ	↑					↓				
m	-2	-1	0	1	2	-2	-1	0	1	2
occupancy	**0**	**1**	**1**	**0**	**0**	**1**	**0**	**0**	**1**	**0**

$= \mathbf{402}$

Since the occupancy of each quantum state can only be 0 or 1 due to the Pauli Principle, we can read the occupancies as a binary representation of a positive integer. Since the transformation from binary to decimal and vice-versa is unique, every such distribution will correspond to a unique non-negative integer, which we denote as a *configuration.* The basis states can then be simply stored using configurations, without needing to store the entire sequences of 0s and 1s.

The function for building all the basis states - `Setup_Basis()` - uses the orbital angular momentum l and the number of electrons N as inputs. For building the entire basis, we first calculate the maximum and minimum integers that could be configurations for a state with N electrons. Then, we traverse through all the integers in between and count the number of particles in the state represented by each configuration. Any configuration which has N electrons is added to the configuration array. For future use, we also build an array that uses the configuration to point to its index in the configuration array.

```
unsigned long max_confg = 0, min_confg = 0;

// Find maximum and minimum possible configuration
// formed by the distribution of N electrons in 2*(2*l+1) orbitals
// max_confg = 111...000 -> integer
// min_confg = 000...111 -> integer
// no. of 1s = no. of particles ; no. of zeros = 2*(2*l+1)-no. of particles
for ( int ii = 0; ii < n_tot; ii++ ) {
  max_confg+= 1<<( 4 * l_no + 1 - ii );
  min_confg+= 1<<ii;  }

// Initialise the array of indices
for ( unsigned long ii = 0; ii <= max_confg; ii++ ) {
  basis_index.push_back( -1 ); }   // Insert -1 in the array if `ii` is not a basis state

// Fill both arrays
for ( unsigned long ii = min_confg; ii <= max_confg; ii++ ) {
  if ( Particle_Count( l_no, ii ) == n_tot ) {
    basis.push_back( ii );
    basis_index[ii] = ( basis.size()-1 );  } }
```

Listing 5.1: Basis setup

5.2. Angular Momentum Operators in Second Quantisation

We need to identify the representation of all the angular momentum operators in second quantised creation and annihilation operators. For this purpose, we will need to use the ladder operators for angular momentum which we discussed in section 3. For the orbital angular momentum operator $\hat{\mathbf{L}}$, we have the following [8]

$$\begin{aligned}
\hat{L}_z &= \sum_{m_L=-L}^{L} \sum_{\{\sigma\}} m_L \cdot c^{\dagger}_{m_L,\sigma} c_{m_L,\sigma} \\
\hat{L}_+ &= \sum_{m_L=-L}^{L-1} \sum_{\{\sigma\}} \sqrt{(L-m_L)\,(L+m_L+1)} \cdot c^{\dagger}_{m_L+1,\sigma} c_{m_L,\sigma} \\
\hat{L}_- &= \sum_{m_L=-L+1}^{L} \sum_{\{\sigma\}} \sqrt{(L+m_L)\,(L-m_L+1)} \cdot c^{\dagger}_{m_L-1,\sigma} c_{m_L,\sigma}
\end{aligned} \tag{5.3}$$

and similarly for the spin operators

$$\begin{aligned}\hat{S}_z &= \sum_{\sigma=-S}^{S}\sum_{\{m_L\}} \sigma \cdot c^{\dagger}_{m_L,\sigma} c_{m_L,\sigma} \\ \hat{S}_+ &= \sum_{\sigma=-S}^{S-1}\sum_{\{m_L\}} \sqrt{(S-\sigma)(S+\sigma+1)} \cdot c^{\dagger}_{m_L,\sigma+1} c_{m_L,\sigma} \\ \hat{S}_- &= \sum_{\sigma=-S+1}^{S}\sum_{\{m_L\}} \sqrt{(S+\sigma)(S-\sigma+1)} \cdot c^{\dagger}_{m_L,\sigma-1} c_{m_L,\sigma} \qquad (5.4)\end{aligned}$$

From equation 3.8, we know that

$$\hat{\mathbf{J}}^2 = \frac{1}{2}\left(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+\right) + \hat{J}_z^2 \qquad (5.5)$$

Using this, we have an explicit method of calculating the action of the $\hat{\mathbf{L}}^2$, $\hat{L}_z$, $\hat{\mathbf{S}}^2$ and $\hat{S}_z$ operators on our basis states.

5.3. Example: Finding joint eigenvalues and eigenvectors of $\hat{\mathbf{L}}^2$, $\hat{L}_z$, $\hat{\mathbf{S}}$, $\hat{S}_z$ for p^2-shell

The theory of adding two angular momenta can be readily extended to adding more than two angular momenta. Recall from chapter 2 that the electrostatic Hamiltonian commutes with the $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ operators. It can be shown that the electrostatic Hamiltonian is diagonal in the basis of the operators $\hat{\mathbf{L}}^2$, $\hat{L}_z$, $\hat{\mathbf{S}}^2$ and $\hat{S}_z$. The expectation values of these operators can then be used to denote the eigenstates of the electrostatic Hamiltonian. This is done using the so called spectroscopic notation, where each multiplet can be written as

$$\text{multiplicity}\longleftarrow \quad {}^{(2S+1)}L \quad \longrightarrow \text{multiplet name}$$

Rather than using the value of L, it is conventional to use the uppercase alphabet corresponding to that L. $(2S+1)$ gives the multiplicity of that multiplet. The individual eigenstates within that multiplet are then distinguished using the expectation values of $\hat{L}_z$ and $\hat{S}_z$. So in general, we represent any eigenstate using the angular momentum expectation values as $|L, M_L; S, M_S\rangle = |L, M_L\rangle\,|S, M_S\rangle$.

For the p^2 configuration, we need to couple two orbital angular momenta and two spins. Using the theory of adding two angular momenta, we know that the allowed values of L are 0,1 and 2 and those of S are 0 and 1. In principle, we would have 6 multiplets owing to the combination of the three values of L and two values of S. But, we should remember that the many-body wave-function should be antisymmetric. It can be shown that the spin function corresponding to $S = 0$ is antisymmetric while the one with $S = 1$ is symmetric. Similarly for the orbital part, $L = 0$ and $L = 2$ are symmetric while $L = 1$ is antisymmetric. So, only three multiplets are valid and can be then written in the spectroscopic notation as ${}^1D$, ${}^3P$ and ${}^1S$.

Once we know which multiplets exist, we can illustrate the method for finding the joint eigenstates of $\vec{L}$ and $\vec{S}$ using the ladder operators. We start with the eigenstates belonging to the ${}^1D$ multiplet. For the ${}^1D$ states, the value of $L = 2$ and $M_L = -2, -1, 0, 1, 2$. We start with the state with the maximum M_L. This state is represented by $|2, 2\rangle$ in the orbital angular momentum notation. When we attempt to use our basis functions to represent this state, we observe that there is only one basis function which can contribute to the state $|2, 2; S, M_S\rangle$, where the two electrons have opposite spins and occupy the state with the highest m_l - $|001 : 001\rangle$. Also, the spins of the individual electrons are in opposite directions, owing to the Pauli principle, so the $M_S = 0$. The value of $S = 0$. Thus,

$$|2, 2; 0, 0\rangle = |001 : 001\rangle \tag{5.6}$$

This implies that the value of M_S can only be 0.

Now, we can step lower in M_L or M_S using the lowering operators L_- and S_- respectively. Since stepping up or down in M_S is not possible, we use the L_- operator

$$\begin{aligned} L_- |2, 2; 0, 0\rangle &= L_- |001 : 001\rangle &(5.7)\\ &= \left(\sum_{m_l=-l+1}^{l} \sum_{\sigma} \sqrt{(l + m_l)(l - m_l + 1)} a^\dagger_{m_l-1,\sigma} a_{m_l,\sigma} \right) |001 : 001\rangle &(5.8)\\ &= \sqrt{2} \left(|001 : 010\rangle + |010 : 001\rangle\right) &(5.9) \end{aligned}$$

Normalising, we can write

$$|2, 1; 0, 0\rangle = \frac{1}{\sqrt{2}} \left(|001 : 010\rangle + |010 : 001\rangle\right) \tag{5.10}$$

Using this procedure, we can keep applying L_- to obtain the rest of the ${}^1D$ states. The results we obtain are

$$\begin{aligned} |2, 0; 0, 0\rangle &= \frac{1}{\sqrt{3}} \left(|001 : 100\rangle + 2\,|010 : 010\rangle + |100 : 001\rangle\right) &(5.11)\\ |2, -1; 0, 0\rangle &= \frac{1}{\sqrt{2}} \left(|010 : 100\rangle + |100 : 010\rangle\right) &(5.12)\\ |2, -2; 0, 0\rangle &= |100 : 100\rangle &(5.13) \end{aligned}$$

Now we need to find a way to step from the ${}^1D$ states to the ${}^3P$ states. For the ${}^3P$ states, the highest value of M_L is 1. We note that the eigenstates $|2,1;S,0\rangle$ and $|1,1;S,0\rangle$ belong to the same plane in the (M_L, M_S) subspace and are orthogonal to each other. Thus a state orthogonal to the $|2,1;0,0\rangle$ belongs to the ${}^3P$ multiplet. This is calculated to be

$$|1,1;S,0\rangle = \frac{1}{\sqrt{2}}\left(|001:010\rangle - |010:001\rangle\right) \tag{5.14}$$

We can again use $\vec{S}^2$ to calculate that the value of S for this state is 1. Now that we know the expansion for $|1,1;1,0\rangle$, we can use the ladder operators to calculate all nine states belonging to the ${}^3P$ multiplet.

Finally we need to find the single state that belongs to the ${}^1S$. Again, using the argument for orthogonal functions in the (M_L, M_S) subspace, we can deduce that the state $|0,0;0,0\rangle$ is orthogonal to $|2,0;0,0\rangle$ and $|1,0;1,0\rangle$ to give us that

$$|0,0;0,0\rangle = \frac{1}{\sqrt{3}}\left(|001:100\rangle - |100:001\rangle - |010:010\rangle\right) \tag{5.15}$$

5.4. Simultaneous Diagonalisation

We want to use the occupation number basis to represent the various operators that are needed for constructing the Hamiltonian and then identifying the resultant eigenstates. First, to find the eigenstates of the many-body Hamiltonian, we need to write the Hamiltonian in our occupation number basis. We have already described the Coulomb interaction between the electrons in the U-matrix, which we demonstrated in (section 4).

Let us now denote our many-body basis states by $|\varphi\rangle$. As per our discussion in (5), we can, in general, expand $|\varphi\rangle$ in terms of creation operators using equation (5.1) as

$$|\varphi\rangle = c^{\dagger}_{\nu_1} c^{\dagger}_{\nu_2} \dots c^{\dagger}_{\nu_N} |0\rangle \tag{5.16}$$

Then, we can build the electrostatic Hamiltonian matrix($\hat{H}_{ES}$) in the basis of occupation numbers using the many-body basis states and the U-matrix (equation 4.14)

$$\left(\hat{H}_{ES}\right)_{ij} = \langle\varphi'|\,\hat{U}\,|\varphi\rangle \tag{5.17}$$

Since the operation of creation and annihilation operators on the basis states $|\varphi\rangle$ is well defined and the matrix element $U^{m_1 m_2}_{m_3 m_4}$ is given by (equation 4.22), we can explicitly calculate the electrostatic Hamiltonian in the basis of occupation numbers.

The next step is to diagonalise the electrostatic Hamiltonian and identify the multiplets for the given electronic configuration. This is achieved using the Linear Algebra Package(`LAPACK`). Since the Hamiltonian is hermitian, we can use the subroutine `dsyev(...)`, which is the eigensolver for double precision real symmetric matrices. The code for this part of the calculation is shown below. The `Diagonalise_Matrix(...)` routine handles the call to LAPACK and returns the eigenstates and eigenenergies of the input matrix.

```
for ( int ii = 0; ii < basis.size(); ii++ ) {
  for ( int iml1 = -l_no; iml1 <= l_no; iml1++ ) {
    for ( int iml2 = -l_no; iml2 <= l_no; iml2++ ) {
      for ( int iml3 = -l_no; iml3 <= l_no; iml3++ ) {
        for ( int iml4 = -l_no; iml4 <= l_no; iml4++ ) {
          // Spin sums
          for ( int ims1 = 0; ims1 <= 1; ims1++ ) {
            for ( int ims2 = 0; ims2 <= 1; ims2++ ) {
              unsigned long res_confg = basis[ii];
              int           res_sign = 1;

              res_confg = El_Remove(l_no, iml3, ims1, res_confg, &res_sign);
              res_confg = El_Remove(l_no, iml4, ims2, res_confg, &res_sign);
              res_confg = El_Create(l_no, iml2, ims2, res_confg, &res_sign);
              res_confg = El_Create(l_no, iml1, ims1, res_confg, &res_sign);

              if ( res_sign !=0 ) {
                if ( ( iml1+iml2 ) == ( iml3+iml4 ) ) {
                  ES_hamiltonian[basis_index[res_confg]][ii]+= 0.5 * res_sign *
                       U_Matrix_Element( l_no, iml1, iml2, iml3, iml4, F );
} } } } } } } } }

Diagonalise_Matrix( ES_hamiltonian, ES_eigvect, ES_eigval, basis.size(),
    ES_eigenvalues, ES_eigenstates );
```

Listing 5.2: Diagonalisation of $\hat{H}_{ES}$

This operation gives us the energy eigenvalues of the electrostatic Hamiltonian, and in turn the multiplet energies. These eigenvalues are, in general, degenerate. Let us denote the eigenvalues of the Hamiltonian as E_1, E_2,..., E_k. The degeneracy for each eigenvalue is denoted by g_1, g_2,..., g_k and the set of eigenstates belonging to each degenerate eigenvalue is denoted by $\psi^i_1, \psi^i_2, \ldots, \psi^i_{g_i}$. Thus

$$\hat{H}_{ES} \left|\psi^i_j\right\rangle = E_i \left|\psi^i_j\right\rangle \tag{5.18}$$

These eigenvectors can be written as linear combinations of the occupation number basis states φ_n

$$\left|\psi_j^{(i)}\right\rangle = \sum_k a_{jk}^{(i)} \left|\varphi_k\right\rangle \tag{5.19}$$

From the physical point of view, we already know that the electrostatic Hamiltonian can be simultaneously diagonalised with the angular momentum and spin operators $\hat{\mathbf{L}}^2$, $\hat{L}_z$, $\hat{\mathbf{S}}^2$ and $\hat{S}_z$. This means that the eigenstates of the Hamiltonian are, in theory, also eigenstates of the angular momentum and spin operators. So it becomes essential to identify the total angular momentum and spin of these eigenstates to pin-point which specific multiplet each eigenstate belongs to. This also works in code, but we can potentially run into problems for degenerate eigenstates of the Hamiltonian. When the eigenvectors are degenerate, they belong to the same degenerate eigenspace and are hence not unique. This means that the eigenstates of the Hamiltonian are not necessarily the eigenstates of the angular momentum and spin operators. Fortunately for us, we can construct the simultaneous eigenstates by taking the linear combinations of the degenerate eigenstates.

We define a new operator $\hat{\mathcal{O}} = \alpha_1\hat{\mathbf{L}}^2 + \alpha_2\hat{L}_z + \alpha_3\hat{\mathbf{S}}^2 + \alpha_4\hat{S}_z$, where α_i are arbitrary real coefficients. If we now choose a set of degenerate eigenstates of the electrostatic Hamiltonian $\left|\psi_j^{(i)}\right\rangle$, for a given i, as a basis, we can build a matrix representation of $\hat{\mathcal{O}}$ in this basis by simply calculating the matrix elements $\left\langle \psi_j^i \right| \hat{\mathcal{O}} \left| \psi_{j'}^i \right\rangle$. Since we do this for a particular set of degenerate eigenstates, we can drop the label (i). Let us denote the new basis as

$$\left|\varphi'_m\right\rangle \equiv \left|\psi_m^{(i)}\right\rangle \tag{5.20}$$

We can diagonalise $\hat{\mathcal{O}}$ in this basis and find the new eigenvectors $\left|\psi'_{j'}\right\rangle$. If we are able to ensure that all the eigenvalues of the matrix are unique, we can ensure that all the eigenvectors are uniquely defined.

$$\hat{\mathcal{O}} \left|\psi'_{j'}\right\rangle = \lambda \left|\psi'_{j'}\right\rangle \tag{5.21}$$

The eigenvectors diagonalise $\hat{\mathcal{O}}$, and hence it is obvious that λ is given by

$$\begin{aligned}\lambda &= \left\langle\psi'_{j'}\right| \hat{\mathcal{O}} \left|\psi'_{j'}\right\rangle \\ &= \alpha_1 \left\langle\psi'_{j'}\right| \hat{\mathbf{L}}^2 \left|\psi'_{j'}\right\rangle + \alpha_2 \left\langle\psi'_{j'}\right| \hat{L}_z \left|\psi'_{j'}\right\rangle + \alpha_3 \left\langle\psi'_{j'}\right| \hat{\mathbf{S}}^2 \left|\psi'_{j'}\right\rangle + \alpha_4 \left\langle\psi'_{j'}\right| \hat{S}_z \left|\psi'_{j'}\right\rangle \\ &= \alpha_1 L\left(L+1\right) + \alpha_2 M_L + \alpha_1 S\left(S+1\right) + \alpha_2 M_S\end{aligned} \tag{5.22}$$

The eigenstates are really useful to us only if we can enforce that all the eigenvalues λ for a given i are unique. For this purpose, it becomes necessary to choose appropriate values for the parameters α_p. The tuning of the eigenvalues can be done by analysing the minimum gap h_{min} and maximum gap h_{max} between two consecutive eigenvalues of the individual angular momentum operators. From theory, we already know that numerically, the largest eigenvalues will be observed for the $\hat{\mathbf{L}}^2$ operator. One way to ensure that the eigenvalues are distinct, is to choose the coefficients α_i such that the eigenvalues of one operator lie between two consecutive eigenvalues of the other operator. We elaborate on this point using an example. Consider the $\hat{\mathbf{L}}^2$ operator; the minimum gap between two consecutive eigenvalues for this operator will be between $L_1 = 1$ and $L_2 = 0$ (see Fig (5.1). Which means that h_{min} can be simply calculated as

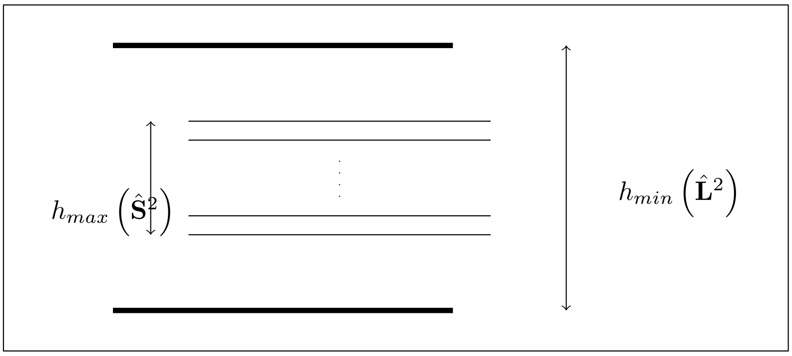

Figure 5.1.: Simultaneous Diagonalisation Example: Method of tuning α_2

$$h_{\text{min}} = L_1\left(L_1 + 1\right) - L_2\left(L_2 + 1\right) = 2 \tag{5.23}$$

For simplicity we set $\alpha_1 = 1$. Next we look at the $\hat{\mathbf{S}}^2$ operator. We now want to tune α_2 such that all the eigenvalues of $\hat{\mathbf{S}}^2$ lie between two consecutive eigenvalues of $\hat{\mathbf{L}}^2$. Seeing as the largest opens shells we are looking at are f-shells, we can deduce that the maximum range for the eigenvalues of $\hat{\mathbf{S}}^2$ will correspond to $S_1 = \frac{7}{2}$ and $S_2 = \frac{1}{2}$

$$h_{\text{max}} = S_1\left(S_1 + 1\right) - S_2\left(S_2 + 1\right) = 30 \tag{5.24}$$

So the problem has been reduced to finding a suitable value of α_2 such that the entire spectrum of $\hat{\mathbf{S}}^2$ lies between consecutive eigenvalues of $\hat{\mathbf{L}}^2$. It is then simple to deduce that $\alpha_2 = \frac{2}{30} = 0.06$. Similarly, we can find the minimum gaps and ranges for the other angular momentum operators as listed in the table below.

Operator	h_{min}	h_{max}	
$\hat{\mathbf{L}}^2$	2	-	$\alpha_1 = 1.00$
$\hat{\mathbf{S}}^2$	2	30	$\alpha_2 = 0.06$
$\hat{L}_z$	1	20	$\alpha_3 = 0.006$
$\hat{S}_z$	1	7	$\alpha_4 = 0.001$

This ensures that the eigenvalues are non-degenerate. These eigenstates are then linear combinations of the basis states $|\varphi_j\rangle$. This leads us to

$$\begin{aligned}
|\psi'_{k'}\rangle &= \sum_m b^{(i)}_{mk'} |\varphi'_m\rangle \\
&= \sum_m b^{(i)}_{mk'} \left|\psi^{(i)}_m\right\rangle \\
&= \sum_m b^{(i)}_{mk'} \left(\sum_k a^{(i)}_{jk} |\varphi_k\rangle\right) \\
&= \sum_m \left(\sum_k b^{(i)}_{mk'} a^{(i)}_{jk} |\varphi_k\rangle\right) \\
&= \sum_k \sum_m b^{(i)}_{mk'} a^{(i)}_{jk} |\varphi_k\rangle \\
&= \sum_k \left(\sum_m b^{(i)}_{mk'} a^{(i)}_{jk}\right) |\varphi_k\rangle \\
&= \sum_k c^{(i)}_{kk'} |\varphi_k\rangle
\end{aligned} \tag{5.25}$$

This gives us the representation of the simultaneous eigenvectors in the basis of occupation numbers. These eigenstates can then be used to identify the multiplets belonging to a particular electronic configuration, since they diagonalise all the necessary operators.

5.5. Basis Transform

When dealing with problems in solid-state physics, we generally describe wave-functions in terms of cubic harmonics, rather than in terms of spherical harmonics. This is because cubic harmonics are real, and much easier to visualise. Another reason to switch to cubic harmonics is the fact that we are going to also look at a simplified version of our electrostatic U-matrix later. This is a popular matrix for Quantum Monte Carlo, and hence much better dealt with using real harmonics.

We approach this task by first transforming the many-body Hamiltonian into a basis of occupation numbers, but this time in the basis of cubic harmonics. From the point of view of the code, the new basis is exactly the same, but conceptually, the occupations denote occupied single particle cubic harmonic states rather than spherical harmonic states.

We define cubic harmonics $X^{\nu}_{k} \equiv |k\nu\rangle$ in terms of the spherical harmonics defined in equation 4.29

$$
\begin{aligned}
|k,-\nu\rangle &= \frac{i}{\sqrt{2}}\left(Y_k^{-\nu} + (-1)^{\nu+1}\,Y_k^{\nu}\right)\\
|k,0\rangle &= Y_k^0\\
|k,\nu\rangle &= \frac{1}{\sqrt{2}}\left(Y_k^{-\nu} + (-1)^{\nu}\,Y_k^{\nu}\right)
\end{aligned}
\tag{5.26}
$$

As a specific example, we look at the p-shell. For $l = 1$, we have the following

$$
\begin{aligned}
|1,-1\rangle &= \frac{i}{\sqrt{2}}\left(Y_1^{-1} + Y_1^{1}\right) = X_1^{-1}\\
|1,0\rangle &= Y_1^0 = X_1^0\\
|1,1\rangle &= \frac{1}{\sqrt{2}}\left(Y_1^{-1} - Y_1^{1}\right) = X_1^{1}
\end{aligned}
\tag{5.27}
$$

This transformation can be represented as a matrix product

$$
\frac{1}{\sqrt{2}}\begin{pmatrix} -i & 0 & -i\\ 0 & \sqrt{2} & 0\\ 1 & 0 & -1 \end{pmatrix}\begin{pmatrix} Y_1^{-1}\\ Y_1^0\\ Y_1^1 \end{pmatrix} = \begin{pmatrix} X_1^{-1}\\ X_1^0\\ X_1^1 \end{pmatrix}
\tag{5.28}
$$

We can then generalise this matrix definition for any value of l. The matrix is denoted by T and can be written as

$$
T = \frac{1}{\sqrt{2}}\begin{pmatrix}
-i & & & & & & (-1)^l\,i\\
 & \ddots & & & & \iddots & \\
 & & -i & & -i & & \\
 & & & \sqrt{2} & & & \\
 & & 1 & & -1 & & \\
 & \iddots & & & & \ddots & \\
1 & & & & & & (-1)^l
\end{pmatrix}
\tag{5.29}
$$

This transformation is unitary and hence, the inverse transformation matrix S is simply

$$
S = T^{-1} = T^{\dagger}
\tag{5.30}
$$

Here we make a note of some notation that will be used in this section. Firstly, to make the transformation laws clear, we will use Einstein's tensor notation. For a fixed value of quantum numbers n, and l, we can write equation 4.22 in the tensor notation

$$\begin{aligned} U^{m_1 m_2}_{m_3 m_4} &= \sum_{k=0}^{\infty} S^{(k)}(nl) \left[\frac{4\pi}{2k+1} \sum_{\mu=-k}^{k} \langle m_1 | k\mu \times m_3 \rangle \langle m_2 \times k\mu | m_4 \rangle \right] \\ &= \langle m_1 m_2 | \hat{U} | m_3 m_4 \rangle \end{aligned} \tag{5.31}$$

The eigenstates in spherical harmonics are denoted by $|m\rangle$. The transformation matrices in this notation look like

$$T \equiv \tau^i_m; \; S \equiv \varrho^m_i \tag{5.32}$$

where the cubic harmonics are labelled by $i = -l, -l+1, \ldots, l-1, l$. Then the cubic harmonics are denoted by $|i\rangle$ and the transformation laws for the bra- and ket- vectors being defined by

$$\begin{aligned} |i\rangle &= \tau^i_m |m\rangle \\ \langle i| &= \langle m| \varrho^m_i \end{aligned} \tag{5.33}$$

Similarly we can also write the transformation laws for the creation and annihilation operators.

$$\begin{aligned} c^\dagger_{i\sigma} &= \tau^i_m c^\dagger_{m\sigma} \\ c_{i\sigma} &= c_{m\sigma} \varrho^m_i \end{aligned} \tag{5.34}$$

Now, we recall the definition of the electrostatic Hamiltonian in second quantisation 5.17

$$
\begin{aligned}
\hat{U} &= \frac{1}{2} \sum_{\{m\}\{\sigma\}} U^{m_1 m_2}_{m_3 m_4} c^{\dagger}_{m_1\sigma} c^{\dagger}_{m_2\sigma'} c_{m_4\sigma'} c_{m_3\sigma} \\
&= \frac{1}{2} \sum_{\{m\}\{\sigma\}\{i\}\{j\}} \left[\varrho^{m_1}_{i_1} \varrho^{m_2}_{i_2} \tau^{i_3}_{m_3} \tau^{i_4}_{m_4} \left\langle i_1 i_2 \right| \hat{U} \left| i_3 i_4 \right\rangle \right] \times \left[\tau^{j_1}_{m_1} \tau^{j_2}_{m_2} \varrho^{m_3}_{j_3} \varrho^{m_4}_{j_4} c^{\dagger}_{j_1\sigma} c^{\dagger}_{j_2\sigma'} c_{j_4\sigma'} c_{j_3\sigma} \right] \\
&= \frac{1}{2} \sum_{\{i\}\{j\}\{\sigma\}} U^{i_1 i_2}_{i_3 i_4} c^{\dagger}_{j_1\sigma} c^{\dagger}_{j_2\sigma'} c_{j_4\sigma'} c_{j_3\sigma} \left[\sum_{\{m\}} \tau^{j_1}_{m_1} \varrho^{m_1}_{i_1} \tau^{j_2}_{m_2} \varrho^{m_2}_{i_2} \tau^{j_3}_{m_3} \varrho^{m_3}_{i_3} \tau^{j_4}_{m_4} \varrho^{m_4}_{i_4} \right] \\
&= \frac{1}{2} \sum_{\{i\}\{j\}\{\sigma\}} U^{i_1 i_2}_{i_3 i_4} c^{\dagger}_{j_1\sigma} c^{\dagger}_{j_2\sigma'} c_{j_4\sigma'} c_{j_3\sigma} \left[\delta^{j_1}_{i_1} \delta^{j_2}_{i_2} \delta^{j_3}_{i_3} \delta^{j_4}_{i_4} \right] \\
&= \frac{1}{2} \sum_{\{i\}\{\sigma\}} U^{i_1 i_2}_{i_3 i_4} c^{\dagger}_{i_1\sigma} c^{\dagger}_{i_2\sigma'} c_{i_4\sigma'} c_{i_3\sigma} \qquad (5.35)
\end{aligned}
$$

Thus the electrostatic potential operator in both bases looks the same. So the only task we need to accomplish is to calculate the integrals $U^{i_1 i_2}_{i_3 i_4}$ from $U^{m_1 m_2}_{m_3 m_4}$. The code to do this is shown in the listing below.

```
for ( int ii1 = -l_no; ii1 <= l_no; ii1++ ) {
  for ( int ii2 = -l_no; ii2 <= l_no; ii2++ ) {
    for ( int ii3 = -l_no; ii3 <= l_no; ii3++ ) {
      for ( int ii4 = -l_no; ii4 <= l_no; ii4++ ) {
        // Spin sums
        for ( int ims1 = 0; ims1 <= 1; ims1++ ) {
          for ( int ims2 = 0; ims2 <= 1; ims2++ ) {
            unsigned long res_confg = basis[ii];
            int           res_sign = 1;

            res_confg = El_Remove( l_no, ii3, ims1, res_confg, &res_sign );
            res_confg = El_Remove( l_no, ii4, ims2, res_confg, &res_sign );
            res_confg = El_Create( l_no, ii2, ims2, res_confg, &res_sign );
            res_confg = El_Create( l_no, ii1, ims1, res_confg, &res_sign );

            if ( res_sign !=0 ) {
              complex<double> u_trafo (0.0, 0.0);

              for ( int im1 = 0; im1 <= 2*l_no; im1++ ) {
              for ( int im2 = 0; im2 <= 2*l_no; im2++ ) {
              for ( int im3 = 0; im3 <= 2*l_no; im3++ ) {
              for ( int im4 = 0; im4 <= 2*l_no; im4++ ) {
                if ( (im1+im2) == (im3+im4) ) {
                  u_trafo = u_trafo + tau[ii1+l_no][im1] * tau[ii2+l_no][im2] *
                       U_Matrix_Element( l_no, im1-l_no, im2-l_no, im3-l_no,
                      im4-l_no, F ) * conj( tau[ii3+l_no][im3] ) * conj( tau[
                      ii4+l_no][im4] ) / 4.0;  } } } } }

              ES_hamiltonian[basis_index[res_confg]][ii]+= 0.5 * res_sign *
                  real( u_trafo );
} } } } } } }
```

Listing 5.3: Transformation of $U^{m_1 m_2}_{m_3 m_4}$ to $U^{i_1 i_2}_{i_3 i_4}$

The process for generating the new many-body basis (using cubic harmonics), constructing the Hamiltonian matrix in this basis ($\hat{H}_{ES}^{cubic}$) and finding the eigenenergies and eigenstates of this matrix is exactly the same as before. This means with small modifications, we can re-use the code we have written before to achieve these goals.

The resultant eigenstates are now in the basis of cubic harmonics, which means that the angular momentum and spin operators which we used before are no longer useful to identify the resulting multiplets. Just like we did for the U-matrix, we will transform the angular momentum operators into the new basis. As an example, we will show how this is done for the $\hat{L}_z$ operator, and then use this method to derive all the other operators.

From 5.3 we know that

$$\hat{L}_z = \sum_{m=-L}^{L} \sum_{\{\sigma\}} m \cdot c_{m\sigma}^{\dagger} c_{m\sigma} \tag{5.36}$$

Using the rules of transformation,

$$\begin{aligned} \hat{L}_z &= \sum_{m=-L}^{L} \sum_{\{\sigma\}} m \cdot \tau_m^i c_{i\sigma}^{\dagger} c_{i'\sigma} \varrho_{i'}^m \\ &= \sum_{\{i\}\{i'\}\{\sigma\}} c_{i\sigma}^{\dagger} c_{i'\sigma} \left(\sum_{m=-L}^{L} m \tau_m^i \varrho_{i'}^m \right) \end{aligned} \tag{5.37}$$

In a similar fashion, we can define the rest of the operators for the new basis

$$\begin{aligned} \hat{L}_+^{cubic} &= \sum_{\{i\}\{i'\}\{\sigma\}} c_{i\sigma}^{\dagger} c_{i'\sigma} \left(\sum_{m=-L}^{L-1} \sqrt{(L-m)(L+m+1)}\, \tau_{m+1}^i \varrho_{i'}^m \right) \\ \hat{L}_-^{cubic} &= \sum_{\{i\}\{i'\}\{\sigma\}} c_{i\sigma}^{\dagger} c_{i'\sigma} \left(\sum_{m=-L+1}^{L} \sqrt{(L+m)(L-m+1)}\, \tau_{m-1}^i \varrho_{i'}^m \right) \end{aligned} \tag{5.38}$$

In case of the spin operators, it is much easier. Since the transformation is independent of spin, the spin operators are identical to the ones in terms of spherical harmonics, but using the cubic creation and annihilation operators. So

$$\begin{aligned}
\hat{S}_z^{cubic} &= \sum_{\sigma=-S}^{S} \sum_{\{i\}} \sigma \cdot c_{i,\sigma}^{\dagger} c_{i,\sigma} \\
\hat{S}_+^{cubic} &= \sum_{\sigma=-S}^{S-1} \sum_{\{i\}} \sqrt{(S-\sigma)(S+\sigma+1)} \cdot c_{i,\sigma+1}^{\dagger} c_{i,\sigma} \\
\hat{S}_-^{cubic} &= \sum_{\sigma=-S+1}^{S} \sum_{\{i\}} \sqrt{(S+\sigma)(S-\sigma+1)} \cdot c_{i,\sigma-1}^{\dagger} c_{i,\sigma} \qquad (5.39)
\end{aligned}$$

These operators can then be used to identify the multiplets appearing in the eigenstates of the electrostatic Hamiltonian.

5.6. Electrostatic Hamiltonian

5.6.1. Multiplet Energies

The procedure we saw above of diagonalising the Hamiltonian can be implemented very easily. The eigenvalues of the diagonalisation of the electrostatic Hamiltonian are of course the energies of the multiplets. The corresponding eigenvectors can then be identified using the angular momentum operators. While calculating the Hamiltonian, we have additional parameters in the form of the Slater Integrals $F^{(k)}$ as seen in equation (4.26). It is common practice to describe the multiplet energies in terms of these parameters. We will perform all the calculations in the basis of cubic harmonics.

The multiplet energies obtained from this execution have been shown in Tables (5.1) and (5.2). In case of the *d*-shell, it will so happen that for some configurations, there will be repeated multiplets. In that case, the eigenspace of the repeated multiplets is degenerate, and needs further diagonalisation. To avoid this, we have noted all the repeated multiplets at the bottom of the table and the energy value is given for a ratio of $F^{[4]}/F^{[2]} \approx 0.652$

5.6.2. Simplified Hamiltonian

We saw in equation (C.1) the expressions for the diagonal elements of the U-matrix. In some calculations, the off diagonal elements of the U-matrix are dropped and only the diagonal elements $U_{m,m',m,m'}$ and $J_{m,m',m',m}$ are considered in the electrostatic Hamiltonian. This is especially popular in Quantum Monte Carlo calculations to make the problem more tractable.

By making only slight modifications in our code, it is possible for us to calculate the energies and wave-functions of this simplified Hamiltonian ($\hat{H}_{ES}^{\text{red}}$). The eigenstates are no

$\mathbf{d}^2$	$F^{[2]}$	$F^{[4]}$
^3F	-0.163	-0.0204
^1D	-0.061	0.0816
^1G	0.081	0.002
^3P	0.143	-0.190
^1S	0.286	0.286

$\mathbf{d}^3$	$F^{[2]}$	$F^{[4]}$
^4F	-0.306	-0.163
^2G	-0.224	0.029
^2P	-0.122	-0.027
^2H	-0.122	-0.027
^4P	0.000	-0.333
^2F	0.184	-0.197
^2D	-0.0052	
^2D	0.0149	

Table 5.1.: Multiplet energies: d^2 (left) and d^3 (right)

longer diagonal in terms of the $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$ operators, meaning L and S are no longer good quantum numbers.

By doing this, it is possible for us to gain an insight into how calculations may be affected due to this simplification. The energies and degeneracies of $\hat{H}_{ES}^{\mathrm{red}}$ are different from those of the full Hamiltonian. These details have been plotted in Fig (5.2) and (5.3).

As is evident, the spectra for the simplified Hamiltonian are very different from those of the full Hamiltonian. Consequently, we would like to have a quantitative measure of this difference. The idea is as follows. We know that the energies of the multiplets are parametrised in terms of the Slater integrals $F^{[k]}$. We know the exact dependence on these parameters for the full Hamiltonian. We would then like to fit the energies of the full Hamiltonian onto the energies of the simplified Hamiltonian via the Slater integrals. We could then achieve different types of fits depending on what kind of application we are dealing with. For example, if the ground state energy is of major significance, then we could tune the parametrised equation for the simplified Hamiltonian to give us the best results for the ground state.

One way of performing this task is to use the moments of the energy spectra that we obtained. The moments of the spectrum help us decide the various characteristics of the distribution of energy levels. As a simple example, we consider the d^2 configuration. We can calculate the n$^{\mathrm{th}}$ moment of the distribution as

$\mathbf{d}^4$	$F^{[2]}$	$F^{[4]}$
^5D	-0.429	-0.429
^3H	-0.347	-0.156
^1I	-0.306	-0.020
^3G	-0.245	-0.213
^3D	-0.102	-0.293
^1F	0.000	-0.190
^3P	-0.019	
^3P	-0.0006	
^1G	-0.013	
^1G	0.003	
^1D	-0.009	
^1D	0.015	
^3F	-0.019	
^3F	-0.001	
^1S	-0.010	
^1S	0.029	

$\mathbf{d}^5$	$F^{[2]}$	$F^{[4]}$
^6S	-0.714	-0.714
^4P	-0.571	-0.238
^4G	-0.510	-0.431
^2I	-0.490	-0.204
^2H	-0.449	-0.068
^4D	-0.367	-0.510
^4F	-0.265	-0.408
^2S	-0.061	-0.442
^2P	0.408	-0.544
^2D	-0.025	
^2D	-0.012	
^2D	0.007	
^2F	-0.024	
^2F	-0.019	
^2G	-0.022	
^2G	-0.008	

Table 5.2.: Multiplet energies: d^4 (left) and d^5 (right)

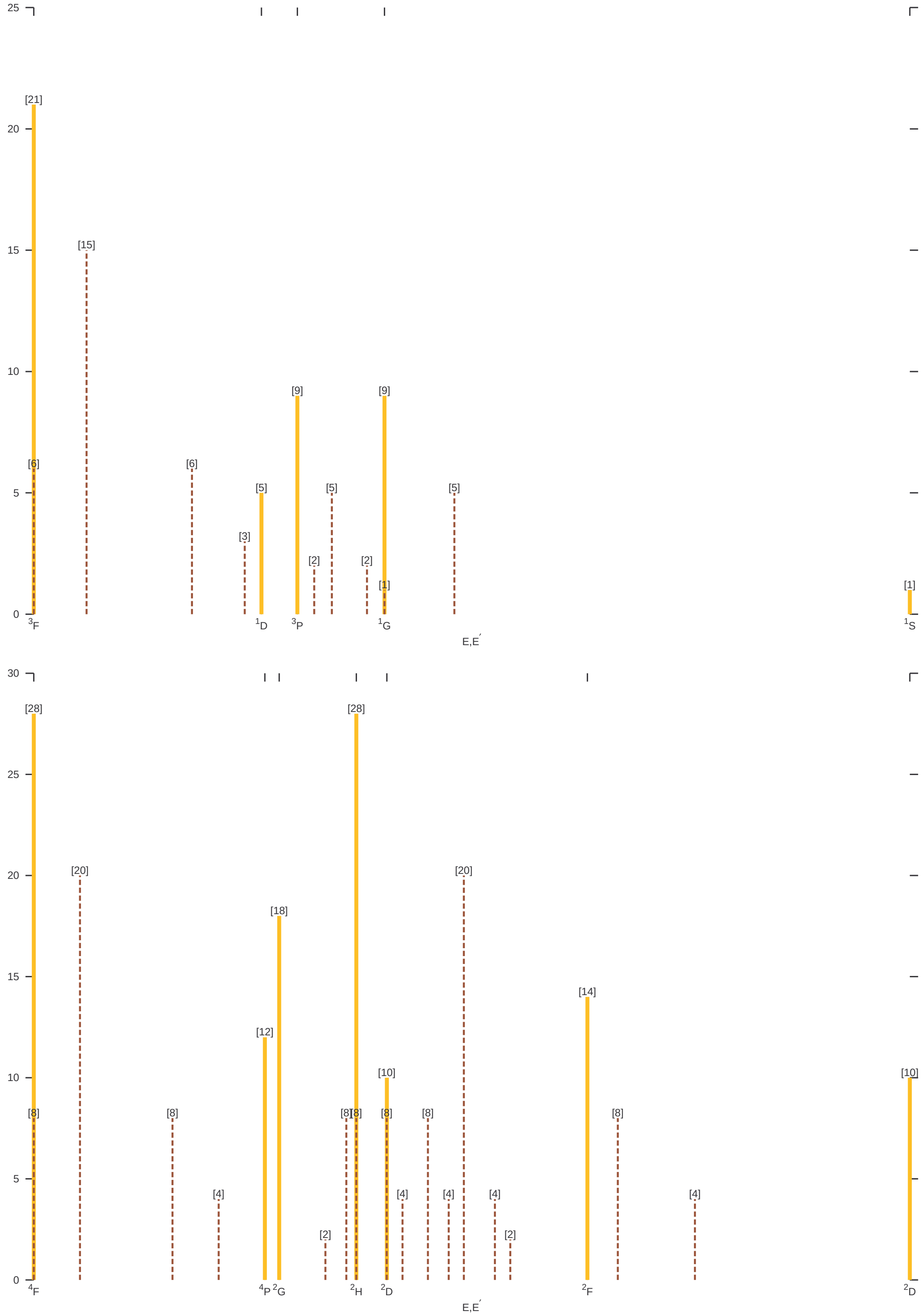

Figure 5.2.: Eigenergies of full Hamiltonian (yellow) and the simplified Hamiltonian (brown) and their corresponding degeneracies: d^2 (above) and d^3 (below). Ratio $F^{[4]}/F^{[2]} \approx 0.652$

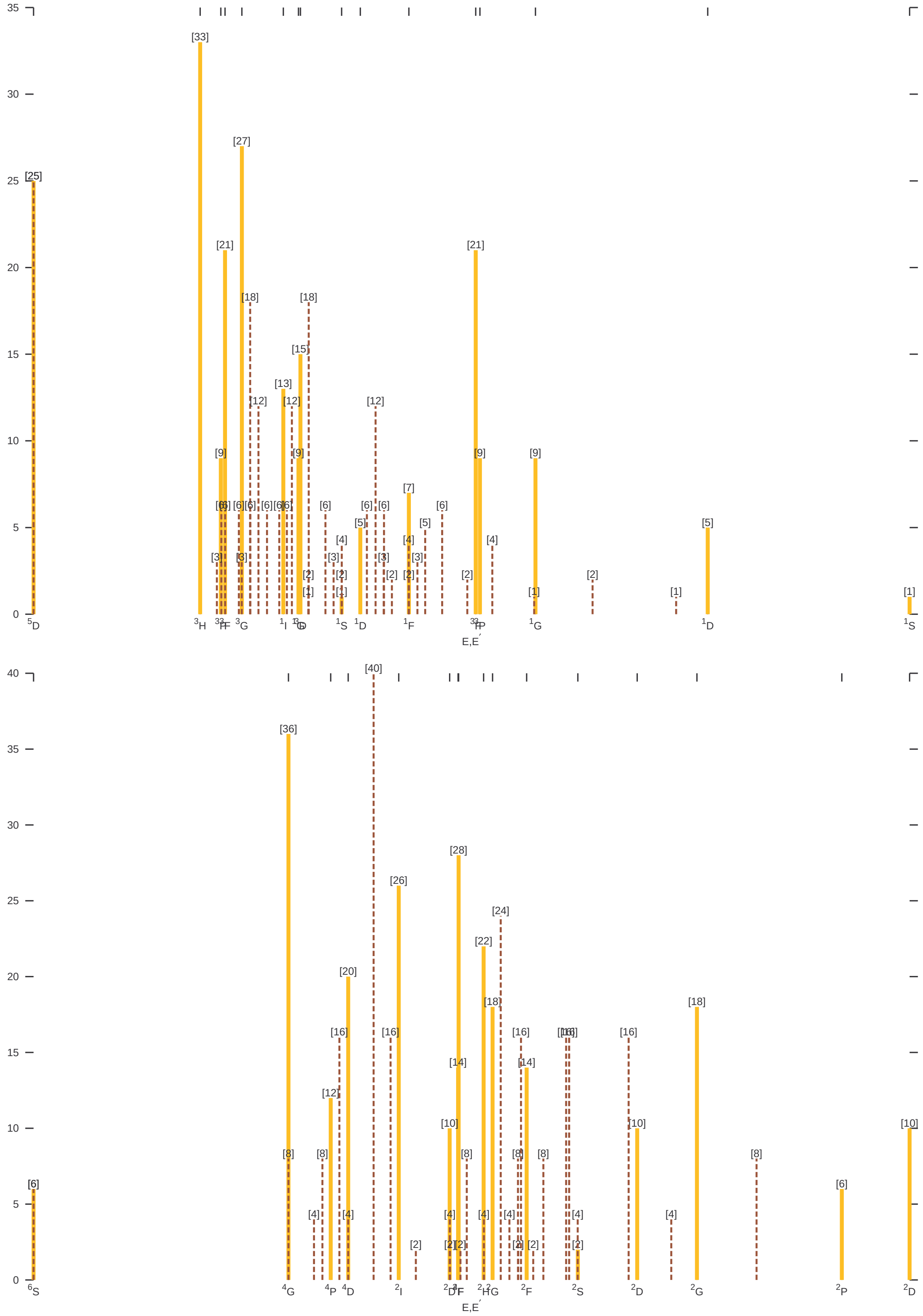

Figure 5.3.: Eigenenergies of the full Hamiltonian (yellow) and the simplified Hamiltonian (brown) and their corresponding degeneracies: d^4 (above) and d^5 (below). Ratio $F^{[4]}/F^{[2]} \approx 0.652$

$$\mu_n = \frac{1}{N}\sum_{i}^{N}(E_i)^n \tag{5.40}$$

where E is the multiplet energy and N is the dimension of the eigenproblem. We will calculate the first three moments of the distributions for the full and the simplified Hamiltonian in terms of the Slater parameters $F^{[2]}$ and $F^{[4]}$

Moment	**Full**		**Simplified**	
	$F^{[2]}$	$F^{[4]}$	$F^{[2]}$	$F^{[4]}$
1	0	0	0	0
2	1.908×10^{-2}	8.998×10^{-3}	7.618×10^{-3}	4.662×10^{-3}
3	-8.142×10^{-4}	-7.754×10^{-4}	-7.813×10^{-4}	-4.524×10^{-4}

Table 5.3.: First three moments of the spectra of the full and the simplified Hamiltonians for the d^2 configuration

We see that the first moments are the same for all. But from the second moment onwards, we see the difference between the full and the simplified Hamiltonian. The idea then is to use these higher order moments to tune the values of $F^{[2]}$ and $F^{[4]}$ so as to suit the problem at hand.

5.7. Crystal Field Term

As we mentioned before, we are only concerned with the electrostatic potential exerted by surrounding ligand atoms on the central metal ion. Since we work completely in the second quantised formulation, we need to describe this interaction in terms of creation and annihilation operators. The electrostatic potential due to the ligands is denoted by $V_{CEF}\left(\nu_i, \nu_j\right)$. Since we assume that n and l are constant, V_{CEF} is just a function of m_i and m_j. Also, this interaction is independent of spin. So transforming this into second quantisation, we can write the crystal field Hamiltonian as

$$\hat{H}_{CEF} = \sum_{m,m'=-l}^{l}\sum_{\sigma} V_{CEF}(m,m')c^{\dagger}_{m,\sigma}c_{m',\sigma} \tag{5.41}$$

The calculation of $V_{CEF}\left(m_1, m_2\right)$ is a separate exercise which we do not discuss here. Our main concern is to see the effect of the crystal field on our electrostatic energy levels. We discuss here the commonly discussed case of an octahedral ligand field around the central atom. We assume that all the ligands possess the same charge and are equidistant from the central atom. Under these assumptions, we can write $V_{CEF}\left(m_1, m_2\right)$ as

$$V_{CEF}\left(m_1, m_2\right) = \frac{I}{6}\begin{pmatrix} 1 & 0 & 0 & 0 & 5 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 5 & 0 & 0 & 0 & 1 \end{pmatrix} \tag{5.42}$$

This matrix has known eigenvalues: I (2-fold degenerate) and $-2I/3$ (3-fold degenerate) [6]. This separation between the two eigenvalues is conventionally referred to as 10Dq and hence the eigenvalues are respectively 6Dq and −4Dq. We can demonstrate how this interaction affects our electrostatic multiplets using *Tanabe-Sugano* diagrams, which plot the energy levels for varying values of the splitting 10Dq. A feature of this interaction is that it reverses under a particle-hole transform i.e. configurations d^n and d^{10-n} split in opposite ways. As an example, we see the crystal field splitting for 4 different configurations in figs. (5.4) and (5.5) below. Once again, we fix the ratio of $F^{(4)}/F^{(2)} \approx 0.652$ for the U-matrix. Then we can vary the value of 10Dq in terms of $F^{(2)}$. It is easy to see that in terms of I, $10\text{Dq} = I/6$. So we essentially vary the magnitude of I from 0 to $0.3F^{(2)}$.

We can see the effect of the particle-hole transformation from the two sets of figures.

5.8. Spin-Orbit Coupling

The final term that we had considered was the spin-orbit coupling term. This is the first case where we will have a direct interaction between the orbital and spin degrees of freedom. The definition of the spin-orbit term is given as a sum over the N electrons [8]

$$\begin{aligned} \hat{H}_{SO} &= \lambda_{SO} \sum_i^N \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i \\ &= \lambda_{SO} \sum_i^N \left[\hat{l}_i^z \hat{s}_i^z + \frac{1}{2}\left(\hat{l}_i^+ \hat{s}_i^- + \hat{l}_i^- \hat{s}_i^+ \right) \right] \end{aligned} \tag{5.43}$$

This can be translated into second quantised form as

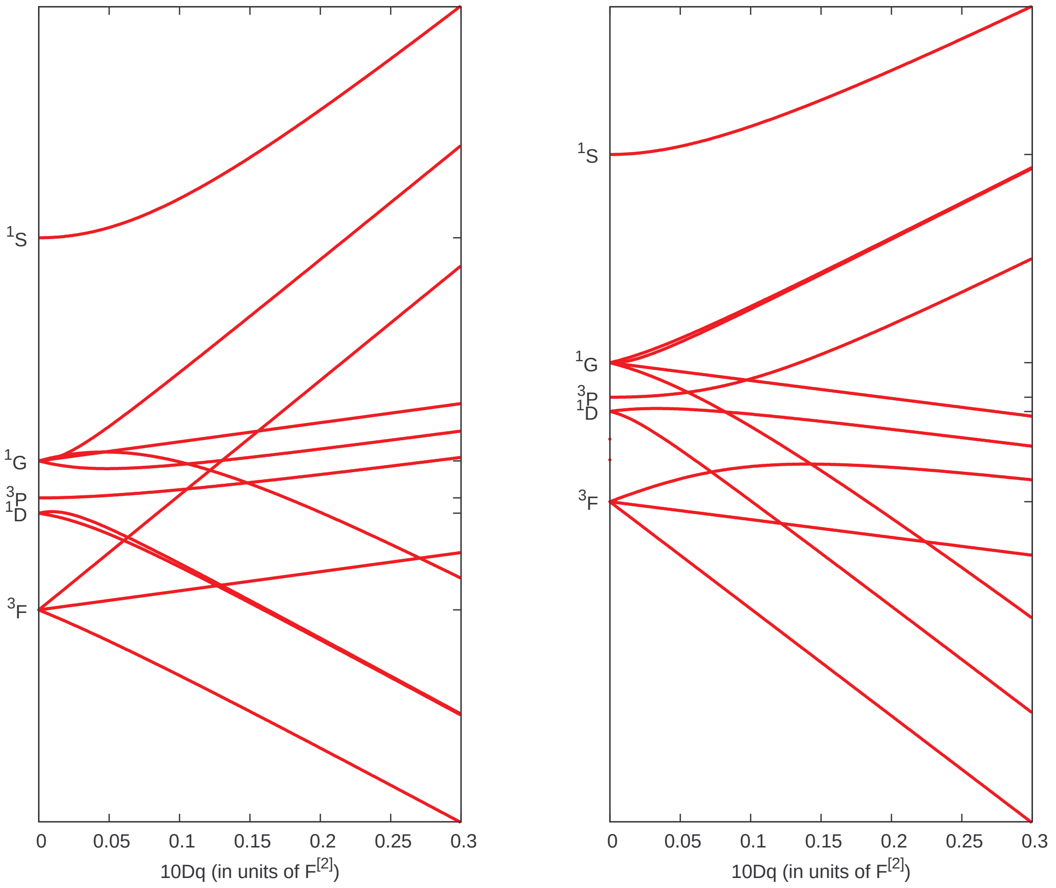

Figure 5.4.: Tanabe-Sugano diagrams for d^2 (left) and d^8. (right)

$$\begin{aligned}\hat{H}_{SO} = {} & \frac{\lambda_{SO}}{2}\sum_{l}^{m=-l}\left[m\left(c^{\dagger}_{m\uparrow}c_{m\uparrow}-c^{\dagger}_{m\downarrow}c_{m\downarrow}\right)\right] \\ & + \frac{\lambda_{SO}}{2}\sum_{l-1}^{m=-l}\left[\sqrt{(l-m)\,(l+m+1)}\left(c^{\dagger}_{m+1,\downarrow}c_{m\uparrow}+c^{\dagger}_{m\uparrow}c_{m+1,\downarrow}\right)\right]\end{aligned} \tag{5.44}$$

The possibility of adding spin-orbit coupling has also been added to the code.

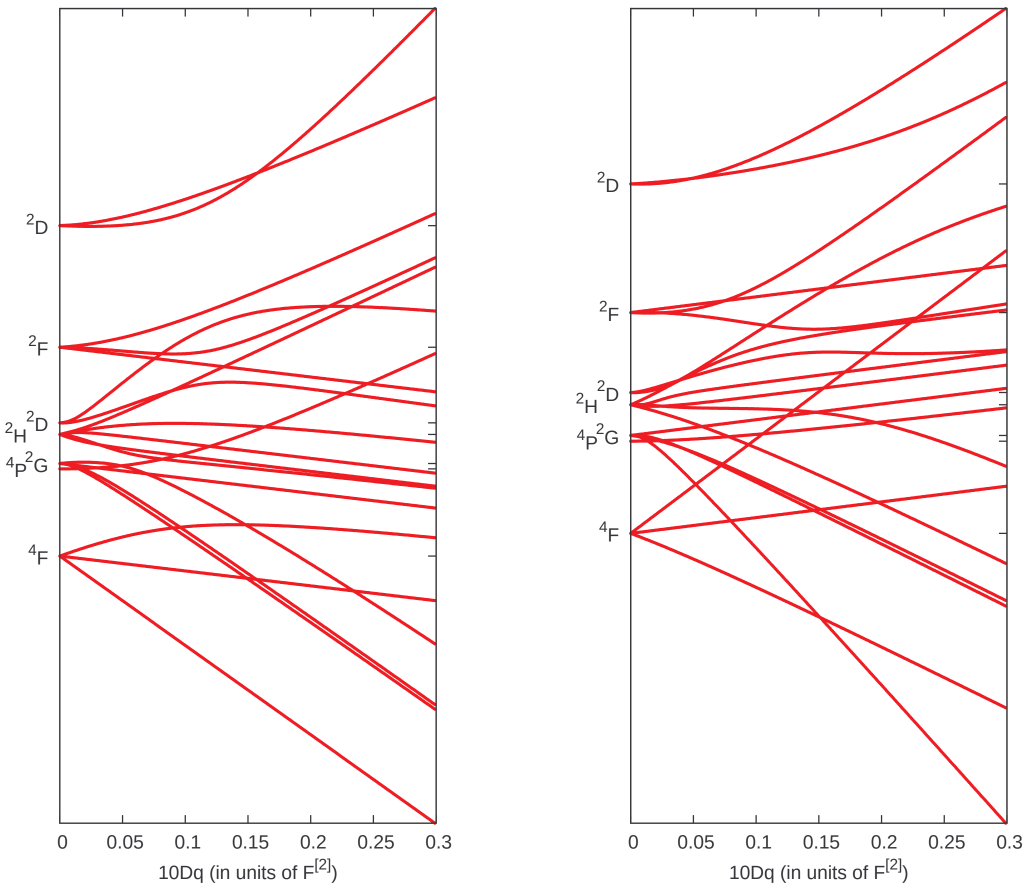

Figure 5.5.: Tanabe-Sugano diagrams for d^3 (left) and d^7. (right)

APPENDIX A

Atomic units

Very often, with problems involving the Schrödinger equation, it becomes difficult to keep track of the various constants and prefactors. To avoid messy calculations, we fix up a system of units where the **numerical values** of certain constants are set to 1. In atomic units (or a.u. for short) we set the values of electron charge e, the electron mass m_e, the Planck's constant $\hbar$ and the dielectric constant $4\pi\varepsilon_0$ to 1. Then we can evaluate all the other quantities such as the atomic units of length, time, energy etc. using dimensional analysis.

The atomic unit of length is a_0 or the Bohr radius which is approximately equal to 5.29×10^{-11}m which is convenient for describing distance at atomic level. Another important unit is the atomic unit of energy, which is called the Hartree, which is approximately equal to 27.211 eV. The energy of the ground state of the free hydrogen atom stands at $-1/2$ Hartree. Thus, these units are very suitable to electronic structure calculations.

APPENDIX B

Gaunt Co-efficient Matrices

The code to obtain the Gaunt Co-efficient Matrices was shown in 4. The output from this was converted to the form of fractions and the data is presented here as matrices $G\left(l,k\right)$. (see also [5]

$$G(1,0) = \frac{1}{\sqrt{4\pi}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$G(1,2) = \frac{1}{\sqrt{20\pi}} \begin{pmatrix} -1 & \sqrt{3} & -\sqrt{6} \\ -\sqrt{3} & 2 & -\sqrt{3} \\ -\sqrt{6} & \sqrt{3} & -1 \end{pmatrix}$$

$$G(2,0) = \frac{1}{\sqrt{4\pi}} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$G(2,2) = \frac{1}{\sqrt{196\pi}} \begin{pmatrix} -\sqrt{20} & \sqrt{30} & -\sqrt{20} & 0 & 0 \\ -\sqrt{30} & \sqrt{5} & \sqrt{5} & -\sqrt{30} & 0 \\ -\sqrt{20} & -\sqrt{5} & \sqrt{20} & -\sqrt{5} & -\sqrt{20} \\ 0 & -\sqrt{30} & \sqrt{5} & \sqrt{5} & -\sqrt{30} \\ 0 & 0 & -\sqrt{20} & \sqrt{30} & -\sqrt{20} \end{pmatrix}$$

$$G(2,4) = \frac{1}{\sqrt{196\pi}} \begin{pmatrix} 1 & -\sqrt{5} & \sqrt{15} & -\sqrt{35} & \sqrt{70} \\ \sqrt{5} & -4 & \sqrt{30} & -\sqrt{40} & \sqrt{35} \\ \sqrt{15} & -\sqrt{30} & 6 & -\sqrt{30} & \sqrt{15} \\ \sqrt{35} & -\sqrt{40} & \sqrt{30} & -4 & \sqrt{5} \\ \sqrt{70} & -\sqrt{35} & \sqrt{15} & -\sqrt{5} & 1 \end{pmatrix}$$

$$G(3,0) = \frac{1}{\sqrt{4\pi}} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$G(3,2) = \frac{1}{\sqrt{180\pi}} \begin{pmatrix} -5 & 5 & -\sqrt{10} & 0 & 0 & 0 & 0 \\ -5 & 0 & \sqrt{15} & -\sqrt{20} & 0 & 0 & 0 \\ -\sqrt{10} & -\sqrt{15} & 3 & \sqrt{2} & -\sqrt{24} & 0 & 0 \\ 0 & -\sqrt{20} & -\sqrt{2} & 4 & -\sqrt{2} & -\sqrt{20} & 0 \\ 0 & 0 & -\sqrt{24} & \sqrt{2} & 3 & -\sqrt{15} & -\sqrt{10} \\ 0 & 0 & 0 & -\sqrt{20} & \sqrt{15} & 0 & -5 \\ 0 & 0 & 0 & 0 & -\sqrt{10} & 5 & -5 \end{pmatrix}$$

$$G(3,4) = \frac{1}{\sqrt{484\pi}} \begin{pmatrix} 3 & -\sqrt{30} & \sqrt{54} & -\sqrt{63} & \sqrt{42} & 0 & 0 \\ \sqrt{30} & -7 & \sqrt{32} & -\sqrt{3} & -\sqrt{14} & \sqrt{70} & 0 \\ \sqrt{54} & -\sqrt{32} & 1 & \sqrt{15} & -\sqrt{40} & \sqrt{14} & \sqrt{42} \\ \sqrt{63} & -\sqrt{3} & -\sqrt{15} & 6 & -\sqrt{15} & -\sqrt{3} & \sqrt{63} \\ \sqrt{42} & \sqrt{14} & -\sqrt{40} & \sqrt{15} & 1 & -\sqrt{32} & \sqrt{54} \\ 0 & \sqrt{70} & -\sqrt{14} & -\sqrt{3} & \sqrt{32} & -7 & \sqrt{30} \\ 0 & 0 & \sqrt{42} & -\sqrt{63} & \sqrt{54} & -\sqrt{30} & 3 \end{pmatrix}$$

$$G(3,6) = \frac{5}{429}\sqrt{\frac{13}{4\pi}} \begin{pmatrix} -1 & \sqrt{7} & -\sqrt{28} & \sqrt{84} & -\sqrt{210} & \sqrt{462} & -\sqrt{924} \\ -\sqrt{7} & 6 & -\sqrt{105} & \sqrt{224} & -\sqrt{378} & \sqrt{504} & -\sqrt{462} \\ -\sqrt{28} & \sqrt{105} & -15 & \sqrt{350} & -\sqrt{420} & \sqrt{378} & -\sqrt{210} \\ -\sqrt{84} & \sqrt{224} & -\sqrt{350} & 20 & -\sqrt{350} & \sqrt{224} & -\sqrt{84} \\ -\sqrt{210} & \sqrt{378} & -\sqrt{420} & \sqrt{350} & -15 & \sqrt{105} & -\sqrt{28} \\ -\sqrt{462} & \sqrt{504} & -\sqrt{378} & \sqrt{224} & -\sqrt{105} & 6 & -\sqrt{7} \\ -\sqrt{924} & \sqrt{462} & -\sqrt{210} & \sqrt{84} & -\sqrt{28} & \sqrt{7} & -1 \end{pmatrix}$$

APPENDIX C

Coulomb Integrals

Recall from 4 that we had defined the direct and exchange terms as

$$U_{\nu\nu'} = U_{mm'} = \sum_{k=0}^{\infty} F^{(k)}\left(nl;nl\right) a^{(k)}\left(lm;lm'\right)$$
$$J_{\nu\nu'} = J_{mm'} = \sum_{k=0}^{\infty} F^{(k)}\left(nl;nl\right) b^{(k)}\left(lm;lm'\right) \tag{C.1}$$

The following tables give the values of the angular integrals for different values of (l,k) in both the spherical and cubic bases. (see also [7])

k	$a^{(k)}_{mm'}$	$b^{(k)}_{mm'}$
0	$\frac{1}{1}\begin{pmatrix}1&1&1&1&1\\1&1&1&1&1\\1&1&1&1&1\\1&1&1&1&1\\1&1&1&1&1\end{pmatrix}$	$\frac{1}{1}\begin{pmatrix}1&0&0&0&0\\0&1&0&0&0\\0&0&1&0&0\\0&0&0&1&0\\0&0&0&0&1\end{pmatrix}$
2	$\frac{1}{49}\begin{pmatrix}4&-2&-4&-2&4\\-2&1&2&1&-2\\-4&2&4&2&-4\\-2&1&2&1&-2\\4&-2&-4&-2&4\end{pmatrix}$	$\frac{1}{49}\begin{pmatrix}4&6&4&0&0\\6&1&1&6&0\\4&1&4&1&4\\0&6&1&1&6\\0&0&4&6&4\end{pmatrix}$
4	$\frac{1}{441}\begin{pmatrix}1&-4&6&-4&1\\-4&16&-24&16&-4\\6&-24&36&-24&6\\-4&16&-24&16&-4\\1&-4&6&-4&1\end{pmatrix}$	$\frac{1}{441}\begin{pmatrix}1&5&15&35&70\\5&16&30&40&35\\15&30&36&30&15\\35&40&30&16&5\\70&35&15&5&1\end{pmatrix}$

Table C.1.: $l = 2$ in the basis of spherical harmonics

k	$a^{(k)}_{mm'}$	$b^{(k)}_{mm'}$
0	$\frac{1}{1}\begin{pmatrix}1&1&1&1&1\\1&1&1&1&1\\1&1&1&1&1\\1&1&1&1&1\\1&1&1&1&1\end{pmatrix}$	$\frac{1}{1}\begin{pmatrix}1&0&0&0&0\\0&1&0&0&0\\0&0&1&0&0\\0&0&0&1&0\\0&0&0&0&1\end{pmatrix}$
2	$\frac{1}{49}\begin{pmatrix}4&-2&-4&-2&4\\-2&1&2&1&-2\\-4&2&4&2&-4\\-2&1&2&1&-2\\4&-2&-4&-2&4\end{pmatrix}$	$\frac{1}{49}\begin{pmatrix}4&3&4&3&0\\3&4&1&3&3\\4&1&4&1&4\\3&3&1&4&3\\0&3&4&3&4\end{pmatrix}$
3	$\frac{1}{441}\begin{pmatrix}36&-4&6&-4&-34\\-4&36&-24&-4&-4\\6&-24&36&-24&6\\-4&-4&-24&36&-4\\-34&-4&6&-4&36\end{pmatrix}$	$\frac{1}{441}\begin{pmatrix}36&20&15&20&35\\20&36&30&20&20\\15&30&36&30&15\\20&20&30&36&20\\35&20&15&20&36\end{pmatrix}$

Table C.2.: $l = 2$ in the basis of cubic harmonics

k	$a^{(k)}_{mm'}$	$b^{(k)}_{mm'}$
0	$\frac{1}{1}\begin{pmatrix}1&1&1&1&1&1&1\\1&1&1&1&1&1&1\\1&1&1&1&1&1&1\\1&1&1&1&1&1&1\\1&1&1&1&1&1&1\\1&1&1&1&1&1&1\\1&1&1&1&1&1&1\end{pmatrix}$	$\frac{1}{1}\begin{pmatrix}1&0&0&0&0&0&0\\0&1&0&0&0&0&0\\0&0&1&0&0&0&0\\0&0&0&1&0&0&0\\0&0&0&0&1&0&0\\0&0&0&0&0&1&0\\0&0&0&0&0&0&1\end{pmatrix}$
2	$\frac{1}{225}\begin{pmatrix}25&-0&-15&-20&-15&-0&25\\-0&0&0&0&0&0&-0\\-15&0&9&12&9&0&-15\\-20&0&12&16&12&0&-20\\-15&0&9&12&9&0&-15\\-0&0&0&0&0&0&-0\\25&-0&-15&-20&-15&-0&25\end{pmatrix}$	$\frac{1}{225}\begin{pmatrix}25&25&10&0&0&0&0\\25&0&15&20&0&0&0\\10&15&9&2&24&0&0\\0&20&2&16&2&20&0\\0&0&24&2&9&15&10\\0&0&0&20&15&0&25\\0&0&0&0&10&25&25\end{pmatrix}$
4	$\frac{1}{1089}\begin{pmatrix}9&-21&3&18&3&-21&9\\-21&49&-7&-42&-7&49&-21\\3&-7&1&6&1&-7&3\\18&-42&6&36&6&-42&18\\3&-7&1&6&1&-7&3\\-21&49&-7&-42&-7&49&-21\\9&-21&3&18&3&-21&9\end{pmatrix}$	$\frac{1}{1089}\begin{pmatrix}9&30&54&63&42&0&0\\30&49&32&3&14&70&0\\54&32&1&15&40&14&42\\63&3&15&36&15&3&63\\42&14&40&15&1&32&54\\0&70&14&3&32&49&30\\0&0&42&63&54&30&9\end{pmatrix}$
6	$\frac{5}{429^2}\begin{pmatrix}1&-6&15&-20&15&-6&1\\-6&36&-90&120&-90&36&-6\\15&-90&225&-300&225&-90&15\\-20&120&-300&400&-300&120&-20\\15&-90&225&-300&225&-90&15\\-6&36&-90&120&-90&36&-6\\1&-6&15&-20&15&-6&1\end{pmatrix}$	$\frac{5}{429^2}\begin{pmatrix}1&7&28&84&210&462&924\\7&36&105&224&378&504&462\\28&105&225&350&420&378&210\\84&224&350&400&350&224&84\\210&378&420&350&225&105&28\\462&504&378&224&105&36&7\\924&462&210&84&28&7&1\end{pmatrix}$

Table C.3.: $l = 3$ in the basis of spherical harmonics

k	$a^{(k)}_{mm'}$	$b^{(k)}_{mm'}$
0	$\frac{1}{1}\begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix}$	$\frac{1}{1}\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$
2	$\frac{1}{225}\begin{pmatrix} 25 & 0 & -15 & -20 & -15 & 0 & 25 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -15 & 0 & 21 & 12 & -3 & 0 & -15 \\ -20 & 0 & 12 & 16 & 12 & 0 & -20 \\ -15 & 0 & -3 & 12 & 21 & 0 & -15 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 25 & 0 & -15 & -20 & -15 & 0 & 25 \end{pmatrix}$	$\frac{1}{450}\begin{pmatrix} 50 & 25 & 10 & 0 & 10 & 25 & 0 \\ 25 & 0 & 15 & 40 & 15 & 0 & 25 \\ 10 & 15 & 42 & 4 & 24 & 15 & 10 \\ 0 & 40 & 4 & 32 & 4 & 40 & 0 \\ 10 & 15 & 24 & 4 & 42 & 15 & 10 \\ 25 & 0 & 15 & 40 & 15 & 0 & 25 \\ 0 & 25 & 10 & 0 & 10 & 25 & 50 \end{pmatrix}$
4	$\frac{1}{1089}\begin{pmatrix} 9 & -21 & 3 & 18 & 3 & -21 & 9 \\ -21 & 84 & -7 & -42 & -7 & 14 & -21 \\ 3 & -7 & 21 & 6 & -19 & -7 & 3 \\ 18 & -42 & 6 & 36 & 6 & -42 & 18 \\ 3 & -7 & -19 & 6 & 21 & -7 & 3 \\ -21 & 14 & -7 & -42 & -7 & 84 & -21 \\ 9 & -21 & 3 & 18 & 3 & -21 & 9 \end{pmatrix}$	$\frac{1}{1089}\begin{pmatrix} 9 & 15 & 48 & 63 & 48 & 15 & 0 \\ 15 & 84 & 23 & 3 & 23 & 35 & 15 \\ 48 & 23 & 21 & 15 & 20 & 23 & 48 \\ 63 & 3 & 15 & 36 & 15 & 3 & 63 \\ 48 & 23 & 20 & 15 & 21 & 23 & 48 \\ 15 & 35 & 23 & 3 & 23 & 84 & 15 \\ 0 & 15 & 48 & 63 & 48 & 15 & 9 \end{pmatrix}$

Table C.4.: $l = 3$ in the basis of cubic harmonics

We mention the last two integrals separately owing to their size

$$a^{(6)}_{mm'} = \frac{5}{429^2}\begin{pmatrix} 463 & -6 & 15 & -20 & 15 & -6 & -461 \\ -6 & 288 & -90 & 120 & -90 & -216 & -6 \\ 15 & -90 & 435 & -300 & 15 & -90 & 15 \\ -20 & 120 & -300 & 400 & -300 & 120 & -20 \\ 15 & -90 & 15 & -300 & 435 & -90 & 15 \\ -6 & -216 & -90 & 120 & -90 & 288 & -6 \\ -461 & -6 & 15 & -20 & 15 & -6 & 463 \end{pmatrix}$$

$$b^{(6)}_{mm'} = \frac{5}{2 \times 429^2}\begin{pmatrix} 926 & 469 & 238 & 168 & 238 & 469 & 924 \\ 469 & 576 & 483 & 448 & 483 & 504 & 469 \\ 238 & 483 & 870 & 700 & 420 & 483 & 238 \\ 168 & 448 & 700 & 800 & 700 & 448 & 168 \\ 238 & 483 & 420 & 700 & 870 & 483 & 238 \\ 469 & 504 & 483 & 448 & 483 & 576 & 469 \\ 924 & 469 & 238 & 168 & 238 & 469 & 926 \end{pmatrix}$$

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