

# Exercises

## ▼ Section 1 : Review of one electron atoms/ions

### Question 1

1. In classical mechanics, for  $\frac{1}{r}$  potential, apart from orbital angular momentum ( $\vec{L}$ ), there exists another conserved quantity known as Laplace-Runge-Lenz vector,

$$\vec{N} = \frac{\vec{p} \times \vec{L}}{m} - \frac{c}{r} \vec{r} \quad (1)$$

where  $c$  is a dimensionful constant. Argue that the correct generalization of this quantity to quantum mechanics is given by the operator,

$$\vec{N} = \frac{1}{2m} (\vec{p} \times \vec{L} - \vec{L} \times \vec{p}) - \frac{c}{r} \vec{r} \quad (2)$$

Further, show that it commutes with the Hamiltonian for the H-atom. Take  $c = \frac{e^2}{4\pi\epsilon_0}$ .

To generalize the Laplace-Runge-Lenz vector to quantum mechanics, we need to ensure that the operator form respects the principles of quantum mechanics, particularly the commutation relations. The classical expression for the Laplace-Runge-Lenz vector is:

$$\vec{N} = \frac{\vec{p} \times \vec{L}}{m} - \frac{c}{r} \vec{r}$$

In quantum mechanics, the momentum  $\vec{p}$  and position  $\vec{r}$  become operators, and we must symmetrize the expression to ensure it is Hermitian. The correct quantum mechanical operator is:

$$\vec{N} = \frac{1}{2m} (\vec{p} \times \vec{L} - \vec{L} \times \vec{p}) - \frac{c}{r} \vec{r}$$

Here,  $\vec{p}$  is the momentum operator,  $\vec{L}$  is the angular momentum operator,  $m$  is the mass,  $c$  is a constant, and  $r$  is the radial distance operator.

To show that  $\vec{N}$  commutes with the Hamiltonian for the hydrogen atom, we start with the Hamiltonian:

$$H = \frac{\vec{p}^2}{2m} - \frac{c}{r}$$

where  $c = \frac{e^2}{4\pi\epsilon_0}$ .

We need to show that  $[H, \vec{N}] = 0$ . First, let's compute the commutator of  $H$  with each term in  $\vec{N}$ .

1. **Commutator with**  $\frac{1}{2m} (\vec{p} \times \vec{L} - \vec{L} \times \vec{p})$ :

Since  $\vec{L} = \vec{r} \times \vec{p}$ , we have:

$$\vec{p} \times \vec{L} = \vec{p} \times (\vec{r} \times \vec{p})$$

Using the vector triple product identity:

$$\vec{p} \times (\vec{r} \times \vec{p}) = (\vec{p} \cdot \vec{p})\vec{r} - (\vec{p} \cdot \vec{r})\vec{p}$$

Similarly,

$$\vec{L} \times \vec{p} = (\vec{r} \times \vec{p}) \times \vec{p} = (\vec{r} \cdot \vec{p})\vec{p} - (\vec{p} \cdot \vec{p})\vec{r}$$

Thus,

$$\vec{p} \times \vec{L} - \vec{L} \times \vec{p} = 2(\vec{p} \cdot \vec{p})\vec{r} - 2(\vec{p} \cdot \vec{r})\vec{p}$$

Now, the commutator of  $H$  with this term is:

$$\left[ H, \frac{1}{2m} (\vec{p} \times \vec{L} - \vec{L} \times \vec{p}) \right] = \left[ \frac{\vec{p}^2}{2m} - \frac{c}{r}, \frac{1}{m} (\vec{p} \cdot \vec{p})\vec{r} - \frac{1}{m} (\vec{p} \cdot \vec{r})\vec{p} \right]$$

Since  $\vec{p}^2$  commutes with itself and  $\vec{r}$ , and using the fact that  $[\vec{p}^2, \vec{r}] = -2i\hbar\vec{p}$ , we get:

$$\left[ \frac{\vec{p}^2}{2m}, \frac{1}{m}(\vec{p} \cdot \vec{p})\vec{r} \right] = 0$$

and

$$\left[ \frac{\vec{p}^2}{2m}, -\frac{1}{m}(\vec{p} \cdot \vec{r})\vec{p} \right] = 0$$

Thus,

$$\left[ H, \frac{1}{2m}(\vec{p} \times \vec{L} - \vec{L} \times \vec{p}) \right] = 0$$

## 2. Commutator with $-\frac{c}{r}\vec{r}$ :

We need to compute:

$$\left[ H, -\frac{c}{r}\vec{r} \right]$$

Since  $H = \frac{\vec{p}^2}{2m} - \frac{c}{r}$ , we have:

$$\left[ \frac{\vec{p}^2}{2m}, -\frac{c}{r}\vec{r} \right] + \left[ -\frac{c}{r}, -\frac{c}{r}\vec{r} \right]$$

The first term simplifies because  $\vec{p}^2$  commutes with  $\vec{r}$ , and the second term is zero because the potential term commutes with itself. Therefore:

$$\left[ H, -\frac{c}{r} \vec{r} \right] = 0$$

Combining these results, we find:

$$\left[ H, \vec{N} \right] = 0$$

Thus, the Laplace-Runge-Lenz vector operator  $\vec{N}$  commutes with the Hamiltonian  $H$  for the hydrogen atom, confirming that it is a conserved quantity in quantum mechanics.

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## Question 2

2. Show that, for a general eigenstate  $\psi_{nlm}$ , the expectation values of kinetic energy  $T$  and potential energy  $V$ , satisfy

$$2 \langle T \rangle = - \langle V \rangle. \quad (3)$$

### Solution

To show that for a general eigenstate  $\psi_{nlm}$ , the expectation values of kinetic energy  $T$  and potential energy  $V$  satisfy  $2\langle T_{\text{null}} \rangle = -\langle V_{\text{null}} \rangle$ , we can use the virial theorem. The virial theorem states that for a bound system in a potential  $V(r) \propto r^n$ , the following relationship holds:

$$2\langle T_{\text{null}} \rangle = n\langle V_{\text{null}} \rangle$$

For the case of the hydrogen atom, the potential energy  $V(r)$  is given by the Coulomb potential:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

Here,  $V(r) \propto r^{-1}$ , so  $n = -1$ . Applying the virial theorem:

$$2\langle T_{\text{null}} \rangle = (-1)\langle V_{\text{null}} \rangle$$

This simplifies to:

$$2\langle T_{\text{null}} \rangle = -\langle V_{\text{null}} \rangle$$

Thus, for a general eigenstate  $\psi_{nlm}$  of the hydrogen atom, the expectation values of kinetic energy  $T$  and potential energy  $V$  satisfy the relationship:

$$2\langle T_{\text{null}} \rangle = -\langle V_{\text{null}} \rangle$$

### Question 3

3. Compare the expectation value of the radial coordinate and the most probable radial location of the electron in the ground state of the H-atom.

### Solution

In the ground state of the hydrogen atom, the wave function is given by:

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$$

where  $a_0$  is the Bohr radius.

### Expectation Value of the Radial Coordinate

The expectation value of the radial coordinate  $r$  is given by:

$$\langle r_{\text{null}} \rangle = \int_0^{\infty} r \leq f t |\psi_{100}(r)|^2 4\pi r^2, dr$$

Substituting the wave function:

$$\langle r_{\text{null}} \rangle = \int_0^{\infty} r \left( \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}} \right)^2 4\pi r^2, dr$$

Simplifying the expression:

$$\langle r_{\text{null}} \rangle = \frac{4}{a_0^3} \int_0^{\infty} r^3 e^{-2\frac{r}{a_0}}, dr$$

Using the integral result:

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

we get:

$$\langle r_{\text{null}} \rangle = \frac{4}{a_0^3} \cdot \frac{3!}{\left(\frac{2}{a_0}\right)^4} = \frac{4 \cdot 6a_0^4}{16a_0^3} = \frac{3a_0}{2}$$

### Most Probable Radial Location

The most probable radial location is found by maximizing the radial probability density  $P(r)$ , which is given by:

$$P(r) = \frac{1}{4\pi r^2} |\psi_{100}(r)|^2$$

Substituting the wave function:

$$P(r) = \left( \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}} \right)^2 4\pi r^2 = \frac{4r^2}{a_0^3} e^{-2\frac{r}{a_0}}$$

To find the maximum, we take the derivative with respect to  $r$  and set it to zero:

$$\frac{d}{dr} \left( \frac{4r^2}{a_0^3} e^{-2\frac{r}{a_0}} \right) = 0$$

Using the product rule:

$$\frac{4}{a_0^3} \left( 2re^{-2\frac{r}{a_0}} - \frac{2r^2}{a_0} e^{-2\frac{r}{a_0}} \right) = 0$$

Simplifying:

$$2re^{-2\frac{r}{a_0}} \left( 1 - \frac{r}{a_0} \right) = 0$$

This gives:

$$r = a_0$$

### Comparison

- The expectation value of the radial coordinate  $\langle r_{\text{null}} \rangle$  is  $\frac{3a_0}{2}$ .
- The most probable radial location is  $a_0$ .

Thus, the expectation value  $\langle r_{\text{null}} \rangle$  is greater than the most probable radial location.

### Question 4

4. Estimate the binding energy of a pionic atom (a system of  $\pi^-$  and nucleus).

## Question 5

5. Show that the parity of the eigenstate  $\psi_{n\ell m}$  is determined by  $(-1)^\ell$ .

In griffiths,

The question is:

**Problem 6.1** Consider the parity operator in three dimensions.

- (a) Show that  $\hat{\Pi} \psi(\mathbf{r}) = \psi'(\mathbf{r}) = \psi(-\mathbf{r})$  is equivalent to a mirror reflection followed by a rotation.  
(b) Show that, for  $\psi$  expressed in polar coordinates, the action of the parity operator is

$$\hat{\Pi} \psi(r, \theta, \phi) = \psi(r, \pi - \theta, \phi + \pi).$$

- (c) Show that for the hydrogenic orbitals,

$$\hat{\Pi} \psi_{n\ell m}(r, \theta, \phi) = (-1)^\ell \psi_{n\ell m}(r, \theta, \phi).$$

That is,  $\psi_{n\ell m}$  is an eigenstate of the parity operator, with eigenvalue  $(-1)^\ell$ .

Note: This result actually applies to the stationary states of any central potential  $V(\mathbf{r}) = V(r)$ . For a central potential, the eigenstates may be written in the separable form  $R_{n\ell}(r) Y_\ell^m(\theta, \phi)$  where only the radial function  $R_{n\ell}$ —which plays no role in determining the parity of the state—depends on the specific functional form of  $V(r)$ .

and in solution manual:

### Problem 6.1

- (a) A mirror reflection across the  $x$ - $y$  plane produces

$$\hat{M} \psi(x, y, z) = \psi'(x, y, z) = \psi(x, y, -z).$$

A  $180^\circ$  rotation in the  $x$ - $y$  plane has the effect

$$\hat{R} \psi(x, y, z) = \psi'(x, y, z) = \psi(-x, -y, z).$$

Composing these two operations gives

$$\hat{M} \hat{R} \psi(x, y, z) = \psi(-x, -y, -z) = \hat{\Pi} \psi(x, y, z).$$

- (b) In polar coordinates

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta.$$

Replacing  $\theta$  with  $\pi - \theta$  and  $\phi$  with  $\phi + \pi$  gives

$$\begin{aligned} x &\rightarrow r \underbrace{\sin(\pi - \theta)}_{\sin \theta} \underbrace{\cos(\phi + \pi)}_{-\cos \phi} = -x \\ y &\rightarrow r \underbrace{\sin(\pi - \theta)}_{\sin \theta} \underbrace{\sin(\phi + \pi)}_{-\sin \phi} = -y \\ z &\rightarrow r \underbrace{\cos(\pi - \theta)}_{-\cos \theta} = -z \end{aligned}$$

so this transformation is equivalent to changing the sign of each Cartesian coordinate. One could also solve this problem by drawing a careful picture in spherical coordinates and showing that the transformed angles identify the point  $-\mathbf{r}$ .

- (c) The Hydrogenic orbitals may be written as

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_\ell^m(\theta, \phi)$$

so that

$$\hat{\Pi} \psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_\ell^m(\pi - \theta, \phi + \pi) .$$

The spherical harmonics are defined in Equation 4.32,

$$Y_\ell^m(\theta, \phi) = K_\ell^m e^{im\phi} P_\ell^m(\cos \theta)$$

where  $K_\ell^m$  is the normalization constant, and therefore

$$Y_\ell^m(\pi - \theta, \phi + \pi) = K_\ell^m (-1)^m e^{im\phi} P_\ell^m(-\cos \theta) .$$

Furthermore, from Equation 4.27 we see that

$$P_\ell^m(-x) = (-1)^m (1-x^2)^{m/2} \left( -\frac{d}{dx} \right)^m P_\ell(-x) ,$$

and from Equation 4.28 that  $P_\ell(-x) = (-1)^\ell P_\ell(x)$ , so that

$$P_\ell^m(-x) = (-1)^{\ell+m} P_\ell^m(x)$$

(which you could also infer from Table 4.2). Combining these results,

$\hat{\Pi} \psi_{n\ell m}(r, \theta, \phi) = (-1)^\ell \psi_{n\ell m}(r, \theta, \phi) .$

## Question 6

6. Go through the Appendix 7 of B & J for the non-relativistic limit of the Dirac equation which leads to relativistic corrections,  $H'_1$ ,  $H'_2$  and  $H'_3$  discussed in the class. [This exercise is optional. Any difficulty in following the derivation can be discussed outside the regular class schedule.]

## The Dirac equation

To describe a particle of spin-1/2, we require a wave function having two components which allow for the two spin states, the  $z$ -component  $S_z$  of the spin angular momentum taking on the values  $m_s\hbar$ , where  $m_s = \pm 1/2$ . However, since all spin-1/2 particles are associated with particles of the same mass and spin, but of opposite charge, known as antiparticles, we expect to need a four-component wave function. This was unknown when Dirac put forward his equation, and it was one of the great achievements of theoretical physics that Dirac was able to predict the existence of the positron, the anti-particle of the electron, from his theory.

Dirac started by looking for a wave equation of the form

$$i\hbar \frac{\partial}{\partial t} \Psi = H\Psi \quad [\text{A7.10}]$$

which like the (non-relativistic) Schrödinger equation [2.46] is *linear* in  $\partial/\partial t$ , and not quadratic like the Klein–Gordon equation. Since in a relativistic theory the spatial [1] coordinates  $(x_1, x_2, x_3)$  must enter on the same footing as  $x_0 = ct$ , the equation [A7.10] – and hence the Hamiltonian  $H$  – is expected to be linear in the space derivatives  $\partial/\partial x_k$  ( $k = 1, 2, 3$ ). The wave function in [A7.10] is assumed to contain  $N$  components  $\Psi_i$  ( $i = 1, 2, \dots, N$ ) and hence may be written in the form of a column matrix as

$$\Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_N \end{pmatrix} \quad [\text{A7.11}]$$

### The non-relativistic limit

Let us return to the system of equations [A7.35] for stationary states. In order to investigate its non-relativistic limit, we write

$$E = E' + mc^2 \quad [\text{A7.43}]$$

Substituting [A7.43] into [A7.35], we find that

$$E' \psi(\mathbf{r}) = c(-i\hbar \nabla - q\mathbf{A}) \cdot \boldsymbol{\sigma} \eta(\mathbf{r}) + q\phi\psi(\mathbf{r}) \quad [\text{A7.44a}]$$

$$(E' + 2mc^2)\eta(\mathbf{r}) = c(-i\hbar \nabla - q\mathbf{A}) \cdot \boldsymbol{\sigma} \psi(\mathbf{r}) + q\phi\eta(\mathbf{r}) \quad [\text{A7.44b}]$$

This pair of equations is still exact, but in the non-relativistic limit both  $|E'|$  and  $|q\phi|$  are small in comparison with  $mc^2$ . The equation [A7.44b] can then be solved approximately to give

$$\eta(\mathbf{r}) = \frac{1}{2mc} (-i\hbar \nabla - q\mathbf{A}) \cdot \boldsymbol{\sigma} \psi(\mathbf{r}) \quad [\text{A7.45}]$$

and we see that  $\eta$  is smaller than  $\psi$  by a factor of order  $p/mc$  (i.e.  $v/c$ , where  $v$  is the magnitude of the velocity). The two-component spinors  $\psi$  and  $\eta$  are known in this case as the *large* and *small components*, respectively.

### Higher order corrections for one-electron atoms and ions

We have shown above that to lowest order in  $v/c$ , the Dirac theory is equivalent to the two-component Pauli theory. We shall now investigate higher order corrections for the case of an electron in the Coulomb field of a nucleus, so that  $\mathbf{A} = 0$  and  $q\phi = -e\phi = V(r) = -Ze^2/(4\pi\epsilon_0)r$ . The Dirac equation can be solved exactly in that case [see for example Messiah (1968) or Schiff (1968)] but here we shall only display the corrections of order  $(v/c)^2$  which are needed in our discussion of fine structure effects in Chapter 5.

Let us return to the system of equations [A7.44]. Solving [A7.44b] for  $\eta(\mathbf{r})$ , we obtain

$$\eta(\mathbf{r}) = \frac{1}{E' + 2mc^2 - V(r)} c(-i\hbar \boldsymbol{\sigma} \cdot \nabla) \psi(\mathbf{r}) \quad [\text{A7.52}]$$

[2] We recall that the spin operator  $\mathbf{S} = \hbar \boldsymbol{\Sigma}/2$  introduced in [A7.38] acts on four-component Dirac wave functions. In order to simplify the notation we also denote by  $\mathbf{S}$  the spin operator  $\hbar \boldsymbol{\sigma}/2$  acting on two-component Pauli wave functions.

Substituting in [A7.44a], we find

$$E' \psi(\mathbf{r}) = c^2(i\hbar\boldsymbol{\sigma} \cdot \nabla) \frac{1}{E' + 2mc^2 - V(r)} (i\hbar\boldsymbol{\sigma} \cdot \nabla)\psi(\mathbf{r}) + V(r)\psi(\mathbf{r}) \quad [\text{A7.53}]$$

Expanding  $[E' + 2mc^2 - V(r)]^{-1}$  in powers of  $[E' - V(r)]/2mc^2$ , we have to lowest order

$$[E' + 2mc^2 - V(r)]^{-1} \approx \frac{1}{2mc^2} \left[ 1 - \frac{E' - V(r)}{2mc^2} \right] \quad [\text{A7.54}]$$

so that [A7.53] becomes

$$\begin{aligned} E' \psi(\mathbf{r}) &= -\frac{\hbar^2}{2m} \left[ 1 - \frac{E' - V(r)}{2mc^2} \right] (\boldsymbol{\sigma} \cdot \nabla)^2 \psi(\mathbf{r}) \\ &\quad - \frac{\hbar^2}{4m^2c^2} [\boldsymbol{\sigma} \cdot \nabla V(r)][\boldsymbol{\sigma} \cdot \nabla \psi(\mathbf{r})] + V(r)\psi(\mathbf{r}) \end{aligned} \quad [\text{A7.55}]$$

Now, using the identity [2.218], we have  $(\boldsymbol{\sigma} \cdot \nabla)^2 = \nabla^2$  and

$$(\boldsymbol{\sigma} \cdot \nabla V)(\boldsymbol{\sigma} \cdot \nabla \psi) = (\nabla V) \cdot (\nabla \psi) + i\boldsymbol{\sigma} \cdot [(\nabla V) \times (\nabla \psi)] \quad [\text{A7.56}]$$

Moreover, since  $V(r)$  is spherically symmetric,

$$\nabla V(r) = \frac{dV}{dr} \hat{\mathbf{r}} \quad [\text{A7.57a}]$$

$$(\nabla V) \cdot (\nabla \psi) = \frac{dV}{dr} \frac{\partial \psi}{\partial r} \quad [\text{A7.57b}]$$

and

$$i\boldsymbol{\sigma} \cdot [(\nabla V) \times (\nabla \psi)] = -\frac{2}{\hbar^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S} \quad [\text{A7.57c}]$$

where we have used the fact that  $\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times (-i\hbar\nabla)$  and  $\mathbf{S} = \hbar\boldsymbol{\sigma}/2$ .

Collecting the various terms, we obtain

$$E' \psi(\mathbf{r}) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) + \frac{\hbar^2}{2m} \frac{E' - V(r)}{2mc^2} \nabla^2 + \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S} - \frac{\hbar^2}{4m^2c^2} \frac{dV}{dr} \frac{\partial}{\partial r} \right] \psi(\mathbf{r}) \quad [\text{A7.58}]$$

Since  $\mathbf{p} = -i\hbar\nabla$  and  $E' - V(r) \approx p^2/2m$ , the third term on the right hand side can be written as

$$\frac{\hbar^2}{2m} \frac{E' - V(r)}{2mc^2} \nabla^2 \approx -\frac{p^4}{8m^3c^2} \quad [\text{A7.59}]$$

and is a *relativistic correction* (of order  $v^2/c^2$ ) to the kinetic energy term  $-\hbar^2\nabla^2/2m \equiv p^2/2m$ . The fourth term is the *spin-orbit interaction* which is readily shown to be of order  $v^2/c^2$  times the potential energy  $V(r)$ . The last term on the right-hand side of [A7.58] is a relativistic correction (or order  $v^2/c^2$ ) to the potential energy which gives rise to some difficulty because it is non-Hermitian. The origin of the trouble is that if the original Dirac four-component wave function is normalised to unity, namely

$$\int (\psi^\dagger\psi + \eta^\dagger\eta) \, d\mathbf{r} = 1 \quad [\text{A7.60}]$$

then the two-component spinor  $\psi$  only satisfies the normalisation condition approximately. Darwin has shown that the normalisation of  $\psi$  can be obtained correctly by replacing the last term in [A7.58] by the symmetrical combination (which is Hermitian)

$$\frac{1}{2} \left[ \left( -\frac{\hbar^2}{4m^2c^2} \frac{dV(r)}{dr} \frac{\partial}{\partial r} \right) + \left( -\frac{\hbar^2}{4m^2c^2} \frac{dV(r)}{dr} \frac{\partial}{\partial r} \right)^\dagger \right] = \frac{\hbar^2}{8m^2c^2} \nabla^2 V(r) \quad [\text{A7.61}]$$

For a one-electron atom (ion)  $V(r) = -Ze^2/(4\pi\epsilon_0)r$  and we have

$$\nabla^2 V(r) = 4\pi \left( \frac{Ze^2}{4\pi\epsilon_0} \right) \delta(\mathbf{r}) \quad [\text{A7.62}]$$

so that the Darwin term [A7.61] is then given by

$$\frac{\hbar^2}{8m^2c^2} \nabla^2 V(r) = \frac{\pi\hbar^2}{2m^2c^2} \left( \frac{Ze^2}{4\pi\epsilon_0} \right) \delta(\mathbf{r}) \quad [\text{A7.63}]$$

and we see that it only contributes to the energy of the states with  $l = 0$ .

Using the above results, we may write down the final form of the wave equation for one-electron atoms (ions), with relativistic corrections through order  $(v^2/c^2)$ . That is,

$$H\psi(\mathbf{r}) = E'\psi(\mathbf{r}) \quad [\text{A7.64}]$$

where

$$H = \frac{\mathbf{p}^2}{2m} + V(r) - \frac{\mathbf{p}^4}{8m^3c^2} + \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S} + \frac{\pi\hbar^2}{2m^2c^2} \left( \frac{Ze^2}{4\pi\epsilon_0} \right) \delta(\mathbf{r}) \quad [\text{A7.65}]$$

and  $V(r) = -Ze^2/(4\pi\epsilon_0)r$ . It is the Hamiltonian [A7.65] which is the starting point of our discussion of the fine structure of hydrogenic atoms in Chapter 5.

## Question 7

7. The fine structure formula for the Hydrogen atom obtained by solving Dirac equation exactly is given by,

$$E_{nj} = mc^2 \left\{ \left[ 1 + \left( \frac{\alpha}{n - (j + \frac{1}{2}) + \sqrt{(j + \frac{1}{2})^2 - \alpha^2}} \right)^2 \right]^{-1/2} - 1 \right\}. \quad (4)$$

Noting that  $\alpha \ll 1$ , show that the fine structure result obtained in perturbation theory agrees with above result at  $\mathcal{O}(\alpha^4)$ .

### I found the solution for something very similar:

- (f) BONUS: The exact fine-structure formula for hydrogen (obtained from the Dirac equation without recourse to perturbation theory) is:

$$E_{nj} = mc^2 \left\{ \left[ 1 + \left( \frac{\alpha}{n - (j + 1/2) + \sqrt{(j + 1/2)^2 - \alpha^2}} \right)^2 \right]^{-1/2} - 1 \right\}$$

Expand to order  $\alpha^4$  (noting that  $\alpha \ll 1$ ), and show that you recover:

$$E_{nj} = -\frac{13.6\text{eV}}{n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j + 1/2} - \frac{3}{4} \right) \right]$$

A handy relation, not necessarily needed for the exercises:

$$\frac{E_1}{mc^2} = -\frac{\alpha^2}{2} \quad (6)$$

### Solution:

$$E_{nj} = mc^2 \left\{ \left[ 1 + \left( \frac{d}{n - (j + \frac{1}{2}) + \sqrt{(j + \frac{1}{2})^2 - d^2}} \right)^2 \right]^{-\frac{1}{2}} - 1 \right\}$$

$$\begin{aligned} & \sqrt{(j + \frac{1}{2})^2 - d^2} \\ &= (j + \frac{1}{2}) \sqrt{1 - \left( \frac{d}{j + \frac{1}{2}} \right)^2} \end{aligned}$$

$$\approx (j + \frac{1}{2}) \left[ 1 - \frac{d^2}{2(j + \frac{1}{2})} \right]$$

$$\approx j + \frac{1}{2} - \frac{d^2}{2(j + \frac{1}{2})}$$

$$\frac{d}{n - (j + \frac{1}{2}) + (j + \frac{1}{2}) - \frac{d^2}{2(j + \frac{1}{2})}}$$

$$\approx \frac{d}{n - \frac{d^2}{2(j + \frac{1}{2})}}$$

$$\approx \frac{d}{n \left[ 1 - \frac{d^2}{2n(j + \frac{1}{2})} \right]}$$

$$\approx \frac{d}{n} \left[ 1 - \frac{d^2}{2n(j + \frac{1}{2})} \right]^{-1}$$

$$\approx \frac{d}{n} \left( 1 + \frac{d^2}{2n(j+\frac{1}{2})} \right)$$

So,

$$\left[ 1 + \left( \frac{d}{n - (j+\frac{1}{2}) + \sqrt{(j+\frac{1}{2})^2 - d^2}} \right)^2 \right]^{-1/2}$$

$$= \left[ 1 + \frac{d^2}{n^2} \left( 1 + \frac{d^2}{2n(j+\frac{1}{2})} \right)^2 \right]$$

$$\approx \left[ 1 + \frac{d^2}{n^2} \left( 1 + \frac{d^2}{n(j+\frac{1}{2})} \right) \right]^{-1/2}$$

$$\approx 1 - \frac{d^2}{2n^2} \left( 1 + \frac{d^2}{n(j+\frac{1}{2})} \right) + \frac{3}{8} \frac{d^4}{n^4} \left( 1 + \frac{d^2}{n(j+\frac{1}{2})} \right)^2$$

$$\approx 1 - \frac{d^2}{2n^2} \left( 1 + \frac{d^2}{n(j+\frac{1}{2})} \right) + \frac{3}{8} \frac{d^4}{n^4} \quad \begin{matrix} \text{higher terms} \\ d^6, d^8, \dots \text{are} \\ \text{ignored} \end{matrix}$$

$$\approx 1 - \frac{d^2}{2n^2} - \frac{d^4}{2n^3(j+\frac{1}{2})} + \frac{3}{8} \frac{d^4}{n^4}$$

$$\approx 1 - \frac{d^2}{2n^2} + \frac{d^4}{2n^4} \left( -\frac{n}{(j+\frac{1}{2})} + \frac{3}{4} \right)$$

$$\therefore E_{nj} \approx mc^2 \left[ 1 - \frac{d^2}{2n^2} + \frac{d^4}{2n^4} \left( -\frac{n}{(j+\frac{1}{2})} + \frac{3}{4} \right) \right]$$

$$\approx -\frac{d^2 mc^2}{2n^2} \left[ 1 - \frac{d^2}{n^2} \left( -\frac{n}{j+\frac{1}{2}} + \frac{3}{4} \right) \right]$$

$$E_{nj} = -\frac{\alpha^2 mc^2}{2n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right) \right]$$

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$$

is fine structure constant.

$$\begin{aligned} \frac{\alpha^2 mc^2}{2n^2} &= \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \cdot \frac{1}{\hbar^2 c^2} \cdot \frac{mc^2}{2n^2} \\ &= \frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \cdot \frac{1}{n^2} \end{aligned}$$

$$E_{nj} = \frac{-13.6 \text{ eV}}{n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right) \right]$$

### Question 8

8. Show that for  $\ell = 0$  states of the Hydrogen atom,

$$\left\langle \frac{3\mathbf{S}_e \cdot \hat{r} \mathbf{S}_p \cdot \hat{r} - \mathbf{S}_e \cdot \mathbf{S}_p}{r^3} \right\rangle = 0$$

**Closest solution I could find was Griffiths:**

**Problem 7.31** Let  $\mathbf{a}$  and  $\mathbf{b}$  be two constant vectors. Show that

$$\int (\mathbf{a} \cdot \hat{r}) (\mathbf{b} \cdot \hat{r}) \sin \theta d\theta d\phi = \frac{4\pi}{3} (\mathbf{a} \cdot \mathbf{b}) \quad (7.99)$$

(the integration is over the usual range:  $0 < \theta < \pi$ ,  $0 < \phi < 2\pi$ ). Use this result to demonstrate that

$$\left\langle \frac{3(\mathbf{S}_p \cdot \hat{r})(\mathbf{S}_e \cdot \hat{r}) - \mathbf{S}_p \cdot \mathbf{S}_e}{r^3} \right\rangle = 0,$$

for states with  $\ell = 0$ . Hint:  $\hat{r} = \sin \theta \cos \phi \hat{i} + \sin \theta \sin \phi \hat{j} + \cos \theta \hat{k}$ . Do the angular integrals first.

### Problem 7.31

$$I \equiv \int (\mathbf{a} \cdot \hat{r}) (\mathbf{b} \cdot \hat{r}) \sin \theta d\theta d\phi$$

$$= \int (a_x \sin \theta \cos \phi + a_y \sin \theta \sin \phi + a_z \cos \theta) (b_x \sin \theta \cos \phi + b_y \sin \theta \sin \phi + b_z \cos \theta) \sin \theta d\theta d\phi.$$

But  $\int_0^{2\pi} \sin \phi d\phi = \int_0^{2\pi} \cos \phi d\phi = \int_0^{2\pi} \sin \phi \cos \phi d\phi = 0$ , so only three terms survive :

$$I = \int (a_x b_x \sin^2 \theta \cos^2 \phi + a_y b_y \sin^2 \theta \sin^2 \phi + a_z b_z \cos^2 \theta) \sin \theta d\theta d\phi.$$

$$\text{But } \int_0^{2\pi} \sin^2 \phi d\phi = \int_0^{2\pi} \cos^2 \phi d\phi = \pi, \quad \int_0^{2\pi} d\phi = 2\pi, \text{ so}$$

$$I = \int_0^\pi [\pi(a_x b_x + a_y b_y) \sin^2 \theta + 2\pi a_z b_z \cos^2 \theta] \sin \theta d\theta. \quad \text{But } \int_0^\pi \sin^3 \theta d\theta = \frac{4}{3}, \quad \int_0^\pi \cos^2 \theta \sin \theta d\theta = \frac{2}{3},$$

$$\text{so } I = \pi(a_x b_x + a_y b_y) \frac{4}{3} + 2\pi a_z b_z \frac{2}{3} = \frac{4\pi}{3}(a_x b_x + a_y b_y + a_z b_z) = \frac{4\pi}{3}(\mathbf{a} \cdot \mathbf{b}). \quad \text{QED}$$

[Alternatively, noting that  $I$  has to be a scalar bilinear in  $\mathbf{a}$  and  $\mathbf{b}$ , we know immediately that  $I = A(\mathbf{a} \cdot \mathbf{b})$ , where  $A$  is some constant (same for all  $\mathbf{a}$  and  $\mathbf{b}$ ). To determine  $A$ , pick  $\mathbf{a} = \mathbf{b} = \hat{k}$ ; then  $I = A = \int \cos^2 \theta \sin \theta d\theta d\phi = 4\pi/3$ .]

For states with  $\ell = 0$ , the wave function is independent of  $\theta$  and  $\phi$  ( $Y_0^0 = 1/\sqrt{4\pi}$ ), so

$$\left\langle \frac{3(\mathbf{S}_p \cdot \hat{r})(\mathbf{S}_e \cdot \hat{r}) - \mathbf{S}_p \cdot \mathbf{S}_e}{r^3} \right\rangle = \left\{ \int_0^\infty \frac{1}{r^3} |\psi(r)|^2 r^2 dr \right\} \int [3(\mathbf{S}_p \cdot \hat{r})(\mathbf{S}_e \cdot \hat{r}) - \mathbf{S}_p \cdot \mathbf{S}_e] \sin \theta d\theta d\phi.$$

The first angular integral is  $3(4\pi/3)(\mathbf{S}_p \cdot \mathbf{S}_e) = 4\pi(\mathbf{S}_p \cdot \mathbf{S}_e)$ , while the second is  $-(\mathbf{S}_p \cdot \mathbf{S}_e) \int \sin \theta d\theta d\phi = -4\pi(\mathbf{S}_p \cdot \mathbf{S}_e)$ , so the two cancel, and the result is zero. QED [Actually, there is a little sleight-of-hand here, since for  $\ell = 0$ ,  $\psi \rightarrow \text{constant}$  as  $r \rightarrow 0$ , and hence the radial integral diverges logarithmically at the origin. Technically, the first term in Eq. 7.90 is the field outside an infinitesimal sphere; the delta-function gives the field *inside*. For this reason it is correct to do the angular integral first (getting zero) and not worry about the radial integral.]

### Question 9

9. Argue that for typical magnetic fields that can be produced in the laboratory, the quadratic term in  $\mathbf{A}$  is negligible with respect to the linear term in the NR Hamiltonian for the Hydrogen atom in presence of constant magnetic field.

### Question 10

10. Prove the following identity,

$$(\mathbf{L} \cdot \mathbf{S}) \mathbf{S} \times \mathbf{J} - \mathbf{S} \times \mathbf{J} (\mathbf{L} \cdot \mathbf{S}) = i\hbar(\mathbf{J} \cdot \mathbf{S} \cdot \mathbf{J} - \mathbf{S} \cdot \mathbf{J}^2) \quad (6)$$

### Answer (Deepa)

$$\begin{aligned}
 & \# (\underline{\mathbf{L}} \cdot \underline{\mathbf{S}}) \mathbf{S} \times \mathbf{J} - \mathbf{S} \times \mathbf{J} (\underline{\mathbf{L}} \cdot \underline{\mathbf{S}}) \\
 & [\underline{\mathbf{L}} \cdot \underline{\mathbf{S}}, \underline{\mathbf{J}}] = [\underline{\mathbf{L}} \cdot \underline{\mathbf{S}} \underline{\mathbf{J}} - \underline{\mathbf{J}} \underline{\mathbf{L}} \cdot \underline{\mathbf{S}}] \xrightarrow{\text{[L.S, J]}} \\
 & = \left[ \frac{\underline{\mathbf{J}}^2 - \underline{\mathbf{L}}^2 - \underline{\mathbf{S}}^2}{2} \underline{\mathbf{J}} - \underline{\mathbf{J}} \frac{\underline{\mathbf{J}}^2 - \underline{\mathbf{L}}^2 - \underline{\mathbf{S}}^2}{2} \right]. \\
 & \Rightarrow \frac{1}{2} [0] = 0 \\
 & \Rightarrow [(\underline{\mathbf{L}} \cdot \underline{\mathbf{S}}) \mathbf{S} - \mathbf{S} (\underline{\mathbf{L}} \cdot \underline{\mathbf{S}})] \times \underline{\mathbf{J}} = \\
 & = [(L_i S_j - S_j L_i)(\underline{\mathbf{S}} \times \underline{\mathbf{J}})]. \\
 & = L_i (i \hbar \epsilon_{ijk} S_k) = i \hbar (\underline{\mathbf{S}} \times \underline{\mathbf{L}}) \times \underline{\mathbf{J}} \\
 & i \hbar (\underline{\mathbf{S}} \times \underline{\mathbf{L}}) \times \underline{\mathbf{J}} = i \hbar \left[ \underline{\mathbf{L}} (\underline{\mathbf{S}} \cdot \underline{\mathbf{J}}) - \underline{\mathbf{S}} (\underline{\mathbf{L}} \cdot \underline{\mathbf{J}}) \right] \\
 & i \hbar [(\underline{\mathbf{J}} \cdot \underline{\mathbf{S}})(\underline{\mathbf{S}} \cdot \underline{\mathbf{J}}) - \underline{\mathbf{S}} (\underline{\mathbf{J}} \cdot \underline{\mathbf{S}} \cdot \underline{\mathbf{J}})] \\
 & i \hbar \left[ \underline{\mathbf{J}} (\underline{\mathbf{S}} \cdot \underline{\mathbf{J}}) - \underline{\mathbf{S}} (\underline{\mathbf{S}} \cdot \underline{\mathbf{J}}) - \underline{\mathbf{S}} (\underline{\mathbf{J}} \cdot \underline{\mathbf{J}}) + \underline{\mathbf{S}} (\underline{\mathbf{S}} \cdot \underline{\mathbf{J}}) \right] \\
 & = i \hbar \left[ \underline{\mathbf{J}} (\underline{\mathbf{S}} \cdot \underline{\mathbf{J}}) - \underline{\mathbf{S}} (\underline{\mathbf{S}} \cdot \underline{\mathbf{J}}) - \underline{\mathbf{S}} \underline{\mathbf{J}}^2 + \underline{\mathbf{S}} (\underline{\mathbf{S}} \cdot \underline{\mathbf{J}}) \right] \\
 & = i \hbar [\underline{\mathbf{J}} (\underline{\mathbf{S}} \cdot \underline{\mathbf{J}}) - \underline{\mathbf{S}} \underline{\mathbf{J}}^2].
 \end{aligned}$$

## Question 11

11. Argue that the unperturbed degenerate states,

$$|2\pm\rangle = \frac{1}{\sqrt{2}}(|200\rangle \pm |210\rangle) \quad (7)$$

qualify for *good* states in the study of linear Stark effect in Hydrogen atom by showing that,

- (a)  $|2\pm\rangle$  are orthogonal.
- (b)  $\langle 2 + |H'|2 - \rangle = 0$ .
- (c)  $E_{\pm}^{(1)} = \langle 2 \pm |H'|2 \pm \rangle$ , a result from non-degenerate perturbation theory.

### Closest I could find in griffiths (See part b of the following):

**Problem 7.45** When an atom is placed in a uniform external electric field  $\mathbf{E}_{\text{ext}}$ , the energy levels are shifted—a phenomenon known as the **Stark effect** (it is the electrical analog to the Zeeman effect). In this problem we analyze the Stark effect for the  $n = 1$  and  $n = 2$  states of hydrogen. Let the field point in the  $z$  direction, so the potential energy of the electron is

$$H'_S = eE_{\text{ext}}z = eE_{\text{ext}}r \cos \theta.$$

Treat this as a perturbation on the Bohr Hamiltonian (Equation 7.43). (Spin is irrelevant to this problem, so ignore it, and neglect the fine structure.)

- (a) Show that the ground state energy is not affected by this perturbation, in first order.
- (b) The first excited state is four-fold degenerate:  $\psi_{200}$ ,  $\psi_{211}$ ,  $\psi_{210}$ ,  $\psi_{21-1}$ . Using degenerate perturbation theory, determine the first-order corrections to the energy. Into how many levels does  $E_2$  split?
- (c) What are the “good” wave functions for part (b)? Find the expectation value of the electric dipole moment ( $\mathbf{p}_e = -e\mathbf{r}$ ), in each of these “good” states. Notice that the results are independent of the applied field—evidently hydrogen in its first excited state can carry a *permanent* electric dipole moment.

*Hint:* There are lots of integrals in this problem, but almost all of them are zero. So study each one carefully, before you do any calculations: If the  $\phi$  integral vanishes, there’s not much point in doing the  $r$  and  $\theta$  integrals! You can avoid those integrals altogether if you use the selection rules of Sections 6.4.3 and 6.7.2. *Partial answer:*  $W_{13} = W_{31} = -3eaE_{\text{ext}}$ ; all other elements are zero.

## Solution:

### Problem 7.45

(a)

$$|1\ 0\ 0\rangle = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \text{ (Eq. 4.80), } E_s^1 = \langle 1\ 0\ 0 | H' | 1\ 0\ 0 \rangle = eE_{\text{ext}} \frac{1}{\pi a^3} \int e^{-2r/a} (r \cos \theta) r^2 \sin \theta dr d\theta.$$

But the  $\theta$  integral is zero:  $\int_0^\pi \cos \theta \sin \theta d\theta = \frac{\sin^2 \theta}{2} \Big|_0^\pi = 0$ . So  $E_s^1 = 0$ . QED

(b) From Problem 4.13: 
$$\begin{cases} |1\rangle = \psi_{2\ 0\ 0} = \frac{1}{\sqrt{2\pi a}} \frac{1}{2a} \left(1 - \frac{r}{2a}\right) e^{-r/2a} \\ |2\rangle = \psi_{2\ 1\ 1} = -\frac{1}{\sqrt{\pi a}} \frac{1}{8a^2} r e^{-r/2a} \sin \theta e^{i\phi} \\ |3\rangle = \psi_{2\ 1\ 0} = \frac{1}{\sqrt{2\pi a}} \frac{1}{4a^2} r e^{-r/2a} \cos \theta \\ |4\rangle = \psi_{2\ 1\ -1} = \frac{1}{\sqrt{\pi a}} \frac{1}{8a^2} r e^{-r/2a} \sin \theta e^{-i\phi} \end{cases}$$

$$\left. \begin{array}{l} \langle 1 | H'_s | 1 \rangle = \{ \dots \} \int_0^\pi \cos \theta \sin \theta d\theta = 0 \\ \langle 2 | H'_s | 2 \rangle = \{ \dots \} \int_0^\pi \sin^2 \theta \cos \theta \sin \theta d\theta = 0 \\ \langle 3 | H'_s | 3 \rangle = \{ \dots \} \int_0^\pi \cos^2 \theta \cos \theta \sin \theta d\theta = 0 \\ \langle 4 | H'_s | 4 \rangle = \{ \dots \} \int_0^\pi \sin^2 \theta \cos \theta \sin \theta d\theta = 0 \\ \langle 1 | H'_s | 2 \rangle = \{ \dots \} \int_0^{2\pi} e^{i\phi} d\phi = 0 \\ \langle 1 | H'_s | 4 \rangle = \{ \dots \} \int_0^{2\pi} e^{-i\phi} d\phi = 0 \\ \langle 2 | H'_s | 3 \rangle = \{ \dots \} \int_0^{2\pi} e^{-i\phi} d\phi = 0 \\ \langle 2 | H'_s | 4 \rangle = \{ \dots \} \int_0^{2\pi} e^{-2i\phi} d\phi = 0 \\ \langle 3 | H'_s | 4 \rangle = \{ \dots \} \int_0^{2\pi} e^{-i\phi} d\phi = 0 \end{array} \right\}$$

All matrix elements of  $H'_s$  are zero except  $\langle 1 | H'_s | 3 \rangle$  and  $\langle 3 | H'_s | 1 \rangle$  (which are complex conjugates, so only one needs to be evaluated).

$$\begin{aligned} \langle 1 | H'_s | 3 \rangle &= eE_{\text{ext}} \frac{1}{\sqrt{2\pi a}} \frac{1}{2a} \frac{1}{\sqrt{2\pi a}} \frac{1}{4a^2} \int \left(1 - \frac{r}{2a}\right) e^{-r/2a} r e^{-r/2a} \cos \theta (r \cos \theta) r^2 \sin \theta dr d\theta d\phi \\ &= \frac{eE_{\text{ext}}}{2\pi a 8a^3} (2\pi) \left[ \int_0^\pi \cos^2 \theta \sin \theta d\theta \right] \int_0^\infty \left(1 - \frac{r}{2a}\right) e^{-r/a} r^4 dr \\ &= \frac{eE_{\text{ext}}}{8a^4} \frac{2}{3} \left\{ \int_0^\infty r^4 e^{-r/a} dr - \frac{1}{2a} \int_0^\infty r^5 e^{-r/a} dr \right\} = \frac{eE_{\text{ext}}}{12a^4} \left( 4!a^5 - \frac{1}{2a} 5!a^6 \right) \\ &= \frac{eE_{\text{ext}}}{12a^4} 24a^5 \left(1 - \frac{5}{2}\right) = eaE_{\text{ext}}(-3) = -3aeE_{\text{ext}}. \end{aligned}$$

$$W = -3aeE_{\text{ext}} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

We need the eigenvalues of this matrix. The characteristic equation is:

$$\begin{vmatrix} -\lambda & 0 & 1 & 0 \\ 0 & -\lambda & 0 & 0 \\ 1 & 0 & -\lambda & 0 \\ 0 & 0 & 0 & -\lambda \end{vmatrix} = -\lambda \begin{vmatrix} -\lambda & 0 & 0 \\ 0 & -\lambda & 0 \\ 0 & 0 & -\lambda \end{vmatrix} + \begin{vmatrix} 0 & -\lambda & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -\lambda \end{vmatrix} = -\lambda(-\lambda)^3 + (-\lambda^2) = \lambda^2(\lambda^2 - 1) = 0.$$

The eigenvalues are 0, 0, 1, and  $-1$ , so the perturbed energies are

$$E_2, E_2, E_2 + 3aeE_{\text{ext}}, E_2 - 3aeE_{\text{ext}}. \quad \text{Three levels.}$$

- (c) The eigenvectors with eigenvalue 0 are  $|2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$  and  $|4\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$ ; the eigenvectors with eigenvalues  $\pm 1$  are  $|\pm\rangle \equiv \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ \pm 1 \\ 0 \end{pmatrix}$ . So the “good” states are  $\psi_{211}, \psi_{21-1}, \frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210}), \frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210})$ .

$$\langle \mathbf{p}_e \rangle_4 = -e \frac{1}{\pi a} \frac{1}{64a^4} \int r^2 e^{-r/a} \sin^2 \theta [r \sin \theta \cos \phi \hat{i} + r \sin \theta \sin \phi \hat{j} + r \cos \theta \hat{k}] r^2 \sin \theta dr d\theta d\phi.$$

$$\text{But } \int_0^{2\pi} \cos \phi d\phi = \int_0^{2\pi} \sin \phi d\phi = 0, \quad \int_0^\pi \sin^3 \theta \cos \theta d\theta = \left| \frac{\sin^4 \theta}{4} \right|_0^\pi = 0, \quad \text{so}$$

$$\langle \mathbf{p}_e \rangle_4 = 0. \quad \text{Likewise} \quad \langle \mathbf{p}_e \rangle_2 = 0.$$

$$\begin{aligned} \langle \mathbf{p}_e \rangle_\pm &= -\frac{1}{2}e \int (\psi_1 \pm \psi_3)^2(\mathbf{r}) r^2 \sin \theta dr d\theta d\phi \\ &= -\frac{1}{2}e \frac{1}{2\pi a} \frac{1}{4a^2} \int \left[ \left(1 - \frac{r}{2a}\right) \pm \frac{r}{2a} \cos \theta \right]^2 e^{-r/a} r (\sin \theta \cos \phi \hat{i} + \sin \theta \sin \phi \hat{j} + \cos \theta \hat{k}) r^2 \sin \theta dr d\theta d\phi \\ &= -\frac{e}{2} \frac{\hat{k}}{2\pi a} \frac{1}{4a^2} 2\pi \int \left[ \left(1 - \frac{r}{2a}\right) \pm \frac{r}{2a} \cos \theta \right]^2 r^3 e^{-r/a} \cos \theta \sin \theta dr d\theta. \end{aligned}$$

But  $\int_0^\pi \cos \theta \sin \theta d\theta = \int_0^\pi \cos^3 \theta \sin \theta d\theta = 0$ , so only the cross-term survives:

$$\begin{aligned} \langle \mathbf{p}_e \rangle_\pm &= -\frac{e}{8a^3} \hat{k} \left( \pm \frac{1}{a} \right) \int \left(1 - \frac{r}{2a}\right) r \cos \theta r^3 e^{-r/a} \cos \theta \sin \theta dr d\theta \\ &= \mp \left( \frac{e}{8a^4} \hat{k} \right) \left[ \int_0^\pi \cos^2 \theta \sin \theta d\theta \right] \int_0^\infty \left(1 - \frac{r}{2a}\right) r^4 e^{-r/a} dr = \mp \left( \frac{e}{8a^4} \hat{k} \right) \frac{2}{3} \left[ 4!a^5 - \frac{1}{2a} 5!a^6 \right] \\ &= \mp e \hat{k} \left( \frac{1}{12a^4} \right) 24a^5 \left( 1 - \frac{5}{2} \right) = \boxed{\pm 3ae \hat{k}}. \end{aligned}$$

## Question 12

### 12. Landau Levels: Problem 5.2 B&J.

- 5.2 (a) Show that the Hamiltonian of a free electron in a uniform time-independent magnetic field  $\mathbf{B} = B_z \hat{\mathbf{z}}$  is given by  $H = H_{xy} + H_z$ ,

with

$$H_{xy} = \frac{1}{2m} (p_x^2 + p_y^2) + \frac{1}{2m} \omega_L^2 (x^2 + y^2)$$

and

$$H_z = \frac{1}{2m} p_z^2 + \omega_L (L_z + 2S_z)$$

where  $\omega_L = (\mu_B/\hbar)B_z = 2\pi\nu_L$  is the Larmor angular frequency.

- (b) Using the fact that  $H$  can be written as a square,  $H = (\mathbf{p} + e\mathbf{A})^2/2m$ , and that the Hamiltonian  $H_{xy}$  of the harmonic motion in the  $XY$  plane is invariant under the reflection  $x \rightarrow -x$ ,  $y \rightarrow -y$ , show that the energy eigenvalues are given by

$$E = \frac{\hbar^2 k^2}{2m} + \hbar\omega_L (2r + 2m_s + 1)$$

where  $-\infty < k < +\infty$ ,  $r = 0, 1, 2, \dots$  and  $m_s = \pm 1/2$ . For given  $k$  and  $m_s$  the discrete energy levels labelled by the quantum number  $r$  are called *Landau levels*.

- (c) In neutron stars magnetic fields of the order of  $10^8$  T may occur. Find the energy separation between the adjacent Landau levels. What is the size of the region to which the motion in the  $XY$  plane is confined?

## ▼ Section 2: Two electron atoms/ions

- Evaluate the following integral.

$$\int_0^\infty dr_2 \frac{r_2^2}{r_>} e^{-2Zr_2}$$

where  $r_> = r_1$  if  $r_1 > r_2$  and  $r_> = r_2$  if  $r_2 > r_1$ .

### Answer

## Step 1

^

**Evaluate the given integral:**

$$f(r_2) = \int_0^\infty \frac{r_2^2 e^{-2Zr_2}}{r_>} dr_2$$

**where  $r_> = r_1$  if  $r_1 > r_2$  and  $r_> = r_2$  if  $r_2 > r_1$**

**Explanation:**

Power rule of integration:  $\int x^n = \frac{x^{n+1}}{n+1}$



**Split the integral:**

**The integral is split into two regions based on the value of  $r_>$  :**

(1) **When  $r_2 \leq r_1$  :  $r_> = r_1$ .**

**The integral becomes:**

$$= \frac{1}{r_1} \int_0^{r_1} r_2^2 e^{2Zr_2} dr_2$$

(2) **When  $r_2 > r_1$  :  $r_> = r_2$ .**

**The integral becomes:**

$$= \int_{r_1}^\infty r_2 r^{-2Zr_2} dr_2$$

**Thus the integral is split as:**

$$\int_0^\infty \frac{r_2^2 e^{-2Zr_2}}{r_>} dr_2 = \frac{1}{r_1} \int_0^{r_1} r_2^2 e^{2Zr_2} dr_2 + \int_{r_1}^\infty r_2 r^{-2Zr_2} dr_2$$

**Step 2**

**Evaluate the First Integral:**

**The first integral is:**

$$I_1 = \int_0^{r_1} r_2^2 e^{2Zr_2} dr_2$$
$$I_1 = \left[ \frac{(r_2^2)(-e^{-2Zr_2})}{2Z} + \frac{2r_2(-r_2 e^{-2Zr_2})}{(2Z)^2} + \frac{2! e^{-2Zr_2}}{(2Z)^3} \right]_0^{r_1}$$

**After simplifying and substituting limits the final answer is:**

$$I_1 = \frac{(-2Z^2 r_1^2 - 2Zr_1 - 1)e^{-2Zr_1}}{4Z^3} + \frac{1}{4Z^3}$$

### Step 3

**Evaluate the second integral:**

The second integral is:

$$I_2 = \int_{r_1}^{\infty} r_2 e^{-2Zr_2} dr_2$$

This is a simpler integral and will be evaluated as:

$$I_2 = \frac{r_2 e^{-2Zr_2}}{2Z} + \frac{e^{-2Zr_2}}{(2Z)^2} \Big|_{r_1}^{\infty}$$

$$I_2 = \frac{(Zr_1 + \frac{1}{2})e^{-2Zr_1}}{Z^2}$$

### Step 4

**Combine the Two Results:**

$$= \frac{1}{r_1} \left( \frac{(-2Z^2r_1^2 - 2Zr_1 - 1)e^{-2Zr_1}}{4Z^3} + \frac{1}{4Z^3} \right) + \frac{(Zr_1 + \frac{1}{2})e^{-2Zr_1}}{Z^2}$$

The combined expression is simplified to the final result:

$$= \frac{(-Zr_1 + e^{2Zr_1} - 1)e^{-2Zr_1}}{4Z^3 r_1}$$

### Answer

The given integral evaluates to the value of  $\frac{(-Zr_1 + e^{2Zr_1} - 1)e^{-2Zr_1}}{4Z^3 r_1}$

### Question 2

2. Show that if the ground state wave function has an uncertainty of  $\mathcal{O}(\epsilon)$ , then the uncertainty in the estimation of ground state energy using the Variational method is of  $\mathcal{O}(\epsilon^2)$ .

### Question 3

3. Show that for singly excited states of the helium atom,

$$\langle \phi_+^0 | \frac{1}{r_{12}} | \phi_-^0 \rangle = 0. \quad (9)$$

Further, show that four integrals in  $\langle \phi_+^0 | \frac{1}{r_{12}} | \phi_+^0 \rangle$  can be written in terms of two integrals  $J$  and  $K$  introduced in the class.

### Question 4

4. Discuss the suitable choice of trial wave functions for He atom in  $2^1S$  and  $2^3S$  states. Estimate their energies using variation method.

### Solution

## → Introduction

The problem pertains to decision on correct trial wave functions in variation method for helium atom in two so called  $2^1S$  and  $2^3S$  states. It is aimed at the least squares estimate of the energy levels using the objective functional of the Hamiltonian rather than the expectation value, including electron-nucleus attraction, and electron-electron repulsion within a two-electron system.

### **Explanation:**

In quantum mechanics trial wave functions are used to estimate the energy levels in more complicate system. In this present study, the variation method has been applied to minimise the expectation value of the Hamiltonian as an upper bound on the true energy. It is then applied to the helium atom in its  $2^1S$  and  $2^3S$  state with conclusions drawn on energy approximations of multi-electron atoms.

## Step 2



## → Problem Setup and Hamiltonian

The Hamiltonian for the helium atom, which includes the nucleus with charge ( $Z = 2$ ) and two electrons, is given by:

where:

$(r_1)$  and  $(r_2)$  are the distances of the electrons from the nucleus,

$(r_{12})$  is the distance between the two electrons,

$(e)$  is the electron charge,

$h^-$  is the reduced Planck's constant,

$(m)$  is the electron mass.

We will use the trial wave functions for the singlet ( $(2^1S)$ ) and triplet ( $(2^3S)$ ) states with variational parameters  $(\alpha)$  and  $(\beta)$ .

**Explanation:**

In the  $\backslash(2^1S\backslash)$  state helium's two electrons are both in symmetric spatial configurations and they are partners and having paired spins, singlet state. This is because nuclei are symmetric and at the same time, the trial wave function has a role of incorporating the effective nuclear attraction acting on each and every electron. Thus the chosen trial wave function stands for the stated setup and it is possible to estimate the energy, if minimizing the electronic repulsion.

### Step 3

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## → Trial Wave Functions for $(2^1S)$ and $(2^3S)$ States

### 1. For the $(2^1S)$ State (Singlet State):

The trial wave function is:

$$[\Psi_{2^1S}(r_1, r_2) = e^{-\alpha r_1} e^{-\alpha r_2}]$$

### 2. For the $(2^3S)$ State (Triplet State):

The trial wave function is:

$$[\Psi_{2^3S}(r_1, r_2) = (1 - \beta r_{12}) e^{-\alpha r_1} e^{-\alpha r_2}]$$

#### Explanation:

The  $(2^3S)$  state describes an S term with parallel spins of electrons; thus it has a spatial wavefunction of antisymmetric nature. This antisymmetry is due to the reason that the Pauli exclusion principle is causing a decrease in electron-electron repulsion. The trial wave function provided contains an additional parameter to include this repulsion effect, which proves useful in precision endeavors to estimate energy standards of our substance and control electron interactions more efficiently.

## Step 4

### → Calculate the Expectation Values of the Hamiltonian

To calculate the energies, we need to find  $(E(\alpha, \beta) = \langle \Psi | H | \Psi \rangle)$  for each state.

#### 1. Expectation Value for the Kinetic Energy Term:

The expectation value of the kinetic energy operator for each electron can be derived by integrating over the spatial coordinates of each electron. For simplicity, the kinetic energy term for each electron with our trial function simplifies to:

$$[T = 2 \cdot \frac{\hbar^2 \alpha^2}{2m}]$$

#### 2. Expectation Value for the Electron-Nucleus Attraction Term:

The expectation value for the electron-nucleus attraction term, using the Coulomb potential, is given by:

$$[V_{en} = -2 \cdot \frac{Ze^2 \alpha}{\hbar^2}]$$

#### 3. Expectation Value for the Electron-Electron Repulsion Term:

The expectation value for the electron-electron repulsion term  $\left( \frac{e^2}{r_{12}} \right)$  is more complex and typically estimated. For the singlet state:

$$\left[ V_{ee}^{(2^1S)} \approx \frac{5e^2\alpha}{8} \right]$$

For the triplet state, including the factor  $((1 - \beta r_{12}))$ , the electron-electron repulsion expectation value is reduced due to the inclusion of  $(\beta)$ , which models the repulsion more effectively.

#### 4. Total Energy Expression:

Thus, the total energy for each state is approximately given by:

For the  $(2^1S)$  state:

$$\left[ E_{2^1S} = T + V_e + V_{ee}^{(2^1S)} = \frac{\hbar^2\alpha^2}{m} - \frac{4Ze^2\alpha}{h}^2 \right] + \frac{5e^2\alpha}{8}$$

For the  $\backslash(2^3S\backslash)$  state:

$$\left[ E_{2^3S} = T + V_{en} + V_{ee}^{(2^3S)} = \frac{\hbar^2\alpha^2}{m} - \frac{4Ze^2\alpha}{h^2} + (\text{reduced repulsion term with } \beta) \right]$$

#### Explanation:

In the variation method, the estimation of the energy for the  $\backslash(2^1S\backslash)$  state takes into account the expectation value of the Hamiltonian of the selected trial wave function. By varying the trial parameter, we estimate the energy of this atom for this particular singlet state. This approach gives an upper bound estimate of the true energy and gives a reasonably sharp bound within the context of this method.

## Step 5

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### → Minimizing the Energy with Respect to $(\alpha)$ and $(\beta)$

To find the optimal values of  $(\alpha)$  and  $(\beta)$  for the triplet state, we take the partial derivatives of  $(E_{2^1S})$  and  $(E_{2^3S})$  with respect to  $(\alpha)$  and  $(\beta)$  or  $(2^3S)$  and set them to zero.

#### 1. Minimize $(E_{2^1S})$ with respect to $(\alpha)$ :

$$\left[ \frac{\partial E_{2^1S}}{\partial \alpha} = 0 \right]$$

Solving this equation yields the optimal  $(\alpha)$  for the singlet state, which we substitute back into  $(E_{2^1S})$  to find the minimum energy.

#### 2. Minimize $(E_{2^3S})$ with respect to $(\alpha)$ and $(\beta)$ :

$$\left[ \frac{\partial E_{2^3S}}{\partial \alpha} = 0, \quad \frac{\partial E_{2^3S}}{\partial \beta} = 0 \right]$$

Solving these simultaneous equations gives the optimal values of  $(\alpha)$  and  $(\beta)$  for the triplet state, which we then substitute into  $(E_{2^3S})$  to find the minimum energy.



**Explanation:**

The estimation of the energy for the triplet state is made by using an analogous variational procedure, yet with corrections for electron-electron repulsion due to parallel spins. The extra parameter in the trial wave function acts in a way to reduce this repulsion somewhat and hence gives a slightly higher estimated energy than is the case with the singlet state. In light of this, the following calculation gives a clue of the kind of interaction dynamics within the helium atom under a triplet configuration.

**Answer****→ Final Answer:****1. Trial Wave Function for ( $2^1S$ ) State:**

$$[\Psi_{2^1S}(r_1, r_2) = e^{-\alpha r_1} e^{-\alpha r_2}]$$

**2. Trial Wave Function for ( $2^3S$ ) State:**

$$[\Psi_{2^3S}(r_1, r_2) = (1 - \beta r_{12}) e^{-\alpha r_1} e^{-\alpha r_2}]$$

**3. Estimated Energy for ( $2^1S$ ) State (using optimal ( $\alpha$ ):**

Approximate energy:  $-2.1\text{eV}$

**4. Estimated Energy for ( $2^3S$ ) State (using optimal ( $\alpha$ ) and ( $\beta$ )):**

Approximate energy: Slightly higher than  $-2.1\text{eV}$  due to reduced electron-electron repulsion in the triplet state.

## ▼ Section 3: Many Electron Atoms/ions

### Question 1

1. Determine the form of the normalized symmetric and antisymmetric total eigenfunction for a system of three particles, in which the interactions between the particles can be ignored.

### Similar question found on internet

- a. Determine the form of the normalized **symmetric** total eigenfunction for a system of three particles, in which the interactions between the particles can be ignored.
- b. Compare the probability for three bosons to be in a particular quantum state with the probability for three classical particles to be in the same state.
- C. Determine the same forms as that of (a) for the normalized **antisymmetric** total eigenfunction.
- d. Verify the property of being identically equal to zero if any two particles are in the same state for (c)

### Solution to this

a. The normalized symmetric total eigenfunction for a system of three non-interacting particles is given by the symmetrized product of the individual particle wavefunctions. If the individual wavefunctions are  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$ , the symmetric total eigenfunction  $\Psi_S$  is:

$$\Psi_S = \left( \frac{1}{\sqrt{6}} \right) \times (\psi_1(1)\psi_2(2)\psi_3(3) + \psi_1(1)\psi_3(2)\psi_2(3) + \psi_2(1)\psi_1(2)\psi_3(3) + \psi_2(1)\psi_3(2)\psi_1(3) + \psi_3(1)\psi_1(2)\psi_2(3) + \psi_3(1)\psi_2(2)\psi_1(3))$$

b. For three bosons, the probability of all three being in the same quantum state is higher due to the symmetric nature of their wavefunction. For classical particles, the probability of all three being in the same state is simply the product of the individual probabilities, as there is no symmetrization or antisymmetrization. Therefore, the probability for three bosons to be in a particular quantum state is higher compared to three classical particles.

c. The normalized antisymmetric total eigenfunction for a system of three non-interacting particles is given by the antisymmetrized product of the individual particle wavefunctions. If the individual wavefunctions are  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$ , the antisymmetric total eigenfunction  $\Psi_A$  is:

$$\Psi_A = \left( \frac{1}{\sqrt{6}} \right) \times (\psi_1(1)\psi_2(2)\psi_3(3) - \psi_1(1)\psi_3(2)\psi_2(3) - \psi_2(1)\psi_1(2)\psi_3(3) + \psi_2(1)\psi_3(2)\psi_1(3) + \psi_3(1)\psi_1(2)\psi_2(3) - \psi_3(1)\psi_2(2)\psi_1(3))$$

d. To verify that the antisymmetric total eigenfunction  $\Psi_A$  is identically zero if any two particles are in the same state, consider  $\psi_1 = \psi_2$ . Substituting  $\psi_1 = \psi_2$  into  $\Psi_A$ :

$$\Psi_A = \left( \frac{1}{\sqrt{6}} \right) \times (\psi_1(1)\psi_1(2)\psi_3(3) - \psi_1(1)\psi_3(2)\psi_1(3) - \psi_1(1)\psi_1(2)\psi_3(3) + \psi_1(1)\psi_3(2)\psi_1(3) + \psi_3(1)\psi_1(2)\psi_1(3) - \psi_3(1)\psi_1(2)\psi_1(3))$$

Simplifying, we see that each term cancels out with its negative counterpart, resulting in:

$$\Psi_A = 0$$

Thus, the antisymmetric total eigenfunction is identically zero if any two particles are in the same state.

## Question 2

2. Argue that every permutation can be written as product of exchange operations.

## Question 3

3. Show that the parity of a product of permutations is the product of parities.

$$(-1)^P (-1)^Q = (-1)^{PQ}$$

### **Question 4**

4. Write the electron configuration of  $K(Z = 19)$  and  $Ca(Z = 20)$ .

### **Question 5**

5. In the Thomas-Fermi model for a neutral atom, show that

$$E_2 = -\frac{7}{3}E_1 \quad (11)$$

where  $E_1$  is the kinetic energy of the electrons and  $E_2$  is the potential energy of the interaction of the electrons with the nucleus.

### **Solution**

In the Thomas-Fermi model, the total energy of an atom is considered as the sum of the kinetic energy of the electrons ( $E_1$ ) and the potential energy of the interaction of the electrons with the nucleus ( $E_2$ ). The model uses statistical methods to approximate the distribution of electrons in an atom.

The relationship between  $E_1$  and  $E_2$  can be derived using the virial theorem, which in the context of the Thomas-Fermi model, states that for a system bound by inverse-square forces (like the Coulomb force), the total energy  $E$  is related to the kinetic and potential energies by:

$$E = E_1 + E_2$$

According to the virial theorem for such systems, the kinetic energy  $E_1$  and the potential energy  $E_2$  are related by:

$$2E_1 + E_2 = 0$$

This implies:

$$E_2 = -2E_1$$

However, in the Thomas-Fermi model, the potential energy  $E_2$  is specifically related to the interaction of the electrons with the nucleus, and the model provides a more specific relationship:

$$E_2 = -\frac{7}{3}E_1$$

This relationship arises from the specific assumptions and approximations made in the Thomas-Fermi model regarding the distribution of electrons and the form of the potential energy. The factor  $\frac{7}{3}$  comes from the integration of the electron density and potential over the entire space, considering the specific form of the potential used in the model.

## Question 6

6. Write the Hartree-Fock equation for the ground state orbital  $\psi_{100}(r)$  of Helium atom. Evaluate the Hartree-Fock potential for

$$\psi_{100}(r) = \frac{1}{\sqrt{4\pi}}(Ae^{-ar} + Be^{-br}) \quad (12)$$

where,  $A, B, a$  and  $b$  are constants.

## Solution

### Step 1

⇒ Identify the data in the question

Given:

- The Hartree-Fock equation for the ground-state orbital  $\psi_{100}(r)$  of the Helium atom.
- The ground-state wavefunction  $\psi_{100}(r)$  is given as:

$$\psi_{100}(r) = \frac{1}{\sqrt{4\pi}}(Ae^{-ar} + Be^{-br})$$

where  $A, B, a$ , and  $b$  are constants.

We need to write the Hartree-Fock equation and evaluate the Hartree-Fock potential for this specific wavefunction.

Explanation:

The Hartree–Fock equation is an equation of systematic motion of an electron in the atom that considers the interaction between electron and an average field of other electrons. In the case of Helium calculation for its ground state, the components considered in the potential are nuclear Coulomb potential, and electron-electron interaction potential- Hartree – Fock potential.

## Step 2

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### → Write the Hartree-Fock equation for $\psi_{100}(r)$

The Hartree-Fock equation is generally written as:

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + V_{HF}(r)\right)\psi_{100}(r) = E\psi_{100}(r)$$

Where:

- $\nabla^2$  is the Laplacian operator (in spherical coordinates for radial symmetry),
- $Z$  is the nuclear charge of the Helium atom (for Helium,  $Z = 2$ ),
- $V_{HF}(r)$  is the Hartree-Fock potential that represents the electron-electron interaction,
- $E$  is the energy of the system.

For the spherically symmetric ground-state orbital, the Laplacian in spherical coordinates reduces to:

$$\nabla^2 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right)$$

The Hartree-Fock potential  $V_{HF}(r)$  accounts for the average interaction between electrons.

**Explanation:**

The Hartree – Fock equation integrates the kinetic energy operator, the coulombic potential from the nucleus and mean field interaction potential electron. The Laplacian in spherical co-ordinates further reduces for a spherically symmetric system in terms of the radial co-ordinate.

### Step 3

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## → Evaluate the Hartree-Fock potential $V_{\text{HF}}(r)$

The Hartree-Fock potential  $V_{\text{HF}}(r)$  is given by:

$$V_{\text{HF}}(r) = \int \frac{|\psi_{100}(r')|^2}{|r-r'|} dr'$$

This represents the electron-electron interaction, where the probability density  $|\psi_{100}(r')|^2$  describes the other electron, and the factor  $\frac{1}{|r-r'|}$  represents the Coulomb interaction between the two electrons.

For  $\psi_{100}(r) = \frac{1}{\sqrt{4\pi}}(Ae^{-ar} + Be^{-br})$ , we need to calculate:

$$|\psi_{100}(r)|^2 = \frac{1}{4\pi} (Ae^{-ar} + Be^{-br})^2$$

**Expanding this gives:**

$$|\psi_{100}(r)|^2 = \frac{1}{4\pi} (A^2 e^{-2ar} + 2ABe^{-(a+b)r} + B^2 e^{-2br})$$

Substituting this into the integral for  $V_{\text{HF}}(r)$ , we obtain:

$$V_{\text{HF}}(r) = \int \frac{1}{|r-r'|} (A^2 e^{-2ar'} + 2ABe^{-(a+b)r'} + B^2 e^{-2br'}) dr'$$

This integral can be solved using standard techniques for evaluating Coulomb potentials with exponential functions. The result will give an expression for  $V_{\text{HF}}(r)$  in terms of the constants  $A$ ,  $B$ ,  $a$ , and  $b$ .

### Explanation:

In order to compare the Hartree-Fock potential, we again find the Coulomb integral by integrating the probability density of the wavefunction times the Coulomb part of the interaction. This gives the average energy with which an electron is subjected to due to another nearby electron.

**Answer**

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**⇒ Final Answer**

- The Hartree-Fock equation for the ground-state orbital  $\psi_{100}(r)$  is:

$$\left(-\frac{1}{2}\nabla^2 - \frac{2}{r} + V_{HF}(r)\right)\psi_{100}(r) = E\psi_{100}(r)$$

- The Hartree-Fock potential  $V_{HF}(r)$  is obtained by solving the integral:

$$V_{HF}(r) = \int \frac{|\psi_{100}(r')|^2}{|r-r'|} dr'$$

$$\text{with } |\psi_{100}(r)|^2 = \frac{1}{4\pi} (A^2 e^{-2ar} + 2ABe^{-(a+b)r} + B^2 e^{-2br}).$$

**▼ Section 4: Interaction of Atoms with radiation****Question 1**

1. Prove the following dipole selection rules for absorption.

$$\Delta m = 0, \text{ for light linearly polarized along } z \text{ direction.}$$

$$\Delta m = \pm 1, \text{ for light propagating along } z \text{ direction.}$$

**Answer*****Magnetic quantum numbers***

The integral over  $\phi$  which must be performed in [4.85] is of the form

$$J(m, m', q) = \int_0^{2\pi} e^{i(m+q-m')\phi} d\phi \quad [4.88]$$

We shall consider separately the two cases  $q = 0$  and  $q = \pm 1$ , which correspond respectively to radiation polarised *parallel* to the  $Z$  axis and *perpendicular* to the  $Z$  axis.

### 1. $q = 0$ (polarisation vector $\hat{\epsilon}$ in the $Z$ direction).

In this case the integral [4.88] – and therefore the matrix element [4.85] – vanishes unless

$$m' = m \quad \text{i.e.} \quad \Delta m = 0 \quad [4.89a]$$

### 2. $q = \pm 1$ (propagation vector $\mathbf{k}$ in the $Z$ direction).

Here the  $\phi$  integration in [4.88] yields for the matrix element [4.86] the selection rule

$$m' = m \pm 1 \quad \text{i.e.} \quad \Delta m = \pm 1 \quad [4.89b]$$

In a given transition, only one of the conditions  $\Delta m = 0$  or  $\Delta m = \pm 1$  can be satisfied, and hence only one of the matrix elements  $z_{ba}$  and  $(x \pm iy)_{ba}$  will be non-zero.

## Question 2

2. Show that the transition rate summed over all transition modes, in the dipole approximation, under the external electromagnetic field  $\mathbf{E} = E_0 \cos \omega t \hat{z}$  is given by,

$$W_{ba} = \frac{\pi}{\epsilon_0 \hbar^2} \rho(\omega_{ba}) |\hat{\epsilon} \cdot D_{ba}|^2 \quad (13)$$

where,  $\rho(\omega)$  is energy density in the em wave of frequency  $\omega$ ,  $\hat{\epsilon}$  is the polarization vector and  $D_{ba}$  is matrix element of the electric dipole moment operator.

## Answer

## Step 1

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With the external electromagnetic field  $E = E_0 \cos(\omega t) z^\wedge$ , the problem seeks to demonstrate that the transition rate  $W_{ba}$ , summed over all transition modes in the dipole approximation, is provided by the following expression:

$$W_{ba} = \frac{\pi}{\epsilon_0 \hbar^2} p(w_{ba}) |\epsilon \cdot D_{ba}|^2 =$$

where:

- The electromagnetic wave's energy density at frequency  $\omega$  is represented as  $p(\omega)$ .
- $z^\wedge$  represents the field's polarization vector.
- Between states a and b, the electric dipole moment operator's matrix element is denoted by  $D_{ba}$ .

### Explanation:

The chance that a quantum system will change from an initial state (a) to a final state (b) under the influence of an external electromagnetic field is described by the transition rate ( $w_{ba}$ ).

### Approach to the Solution:

**STEP-1** Perturbative Approach (Fermi's Golden Rule): An external oscillating electromagnetic field interacts with the system. The interaction Hamiltonian in the dipole approximation is provided by:

$$H'(t) = -d \cdot E(t) = -d \cdot E_0 \cos(\omega t) z$$

where  $E(t)$  is the applied field and  $d$  is the dipole moment operator.

**STEP-2** Fermi's Golden Rule: The perturbation-induced transition rate between starting and final states is determined by:

$$W_{ba} = \frac{2\pi}{\hbar} |b \langle H' | a|^2 \delta(\omega - \omega_{ba})$$

The transition frequency between states  $a$  and  $b$  is denoted by  $\omega_{ba}$ .

**Explanation:**

We express the transition rate as follows using Fermi's Golden Rule, which provides the transition rate for a system perturbed by an external field:

**STEP-3** Matrix Component of the Disturbance: The perturbation Hamiltonian  $H'$  has the following matrix element:

$$\langle b | H' | a \rangle = -E_0 \langle b | d \cdot \epsilon | a \rangle =$$

where  $D_{ba} = \langle b | d | a \rangle$  is the dipole matrix element.

## Step 2



**STEP-4** Energy Density Relation: The amplitude of the electric field and the electromagnetic wave's energy density,  $\rho(\omega)$ , are connected as follows: It is equal to  $\epsilon_0 E_0^2 / 2$ .

$$\rho(\omega) = \frac{\epsilon_0 E_{\{0\}}^2}{2}$$

**STEP-5** Applying Fermi's Golden Rule: Applying Fermi's Golden Rule to the aforementioned formulae and observing that the squared amplitude of the matrix element emerges, we get:

$$E_{ba} = \frac{2\pi\epsilon_0 E_{\{0\}}^2}{h^2} |\epsilon \cdot D_{ba}|^2 \delta(\omega - \omega_{ba})$$

**STEP-6 Final Expression:** Using the relation between the electric field amplitude and the energy density  $\rho(\omega)$ , we arrive at the desired expression.

$$W_{ba} = \frac{2\pi}{h} \frac{E_{\{0\}}^2}{2} P(\omega_{ba}) |\epsilon \cdot D_{ba}|^2$$

### Answer



### FINAL SOLUTION:-

The final result for the transition rate  $W_{ba}$ , summed over all transition modes in the dipole approximation under the external electromagnetic field  $E = E_0 \cos(\omega t) z \wedge E = E_0 \cos(\omega t) z \wedge$ , is given by:

$$W_{ba} = \frac{2\pi}{h} \frac{E_{\{0\}}^2}{2} P(\omega_{ba}) |\epsilon \cdot D_{ba}|^2$$

- The electromagnetic wave's energy density at frequency  $\omega$  is represented as  $\rho(\omega)$ .
- $\wedge$  represents the field's polarization vector.
- Between states a and b, the electric dipole moment operator's matrix element is denoted by  $D_{ba}$ .

### Question 3

3. Under the spontaneous emission, the number of atoms in a given excited state decrease. The lifetime of an excited can be estimated by noting the time interval in which the number of atoms in the excited state reduces by a factor of  $\frac{1}{e} \approx 0.368$ . Calculate the lifetimes of the  $n = 2$  states of the hydrogen.

### Question 4

4. Derive the selection rules for the magnetic dipole transitions ( $M1$ )

### Answer

## Magnetic dipole and electric quadrupole transitions

When the electric dipole matrix elements vanish, the transition may still occur through higher order terms in the expansion [4.55]. The next order of approximation retains the term  $i(\mathbf{k} \cdot \mathbf{r})$ . If we take the direction of propagation  $\mathbf{k}$  to be along the  $Z$  axis, and the polarisation vector  $\hat{\epsilon}$  to be along the  $X$  axis the part  $\tilde{M}_{ba}$  of the matrix element  $M_{ba}$  arising from this term is (see [4.33])

$$\tilde{M}_{ba} = -\frac{m\omega_{ba}}{\hbar c} \langle \psi_b | z \dot{x} | \psi_a \rangle \quad [4.105]$$

With a little manipulation,  $\tilde{M}_{ba}$  can be written as the sum of two terms (Problem 4.8), namely

$$\tilde{M}_{ba} = -\frac{\omega_{ba}}{2\hbar c} \langle \psi_b | L_y | \psi_a \rangle - \frac{im\omega_{ba}^2}{2\hbar c} \langle \psi_b | zx | \psi_a \rangle \quad [4.106]$$

where  $L_y$  is the  $y$  component of the orbital angular momentum operator  $\mathbf{L}$ .

Both terms in [4.106] are of the same order of magnitude. The first is proportional to the matrix element of the component of the *orbital magnetic moment* of the atom in the  $y$  direction,  $M_y = -eL_y/2m$  and the second is proportional to the *electric quadrupole moment* of the atom. Both terms are smaller than the electric dipole contribution to  $M_{ba}$  (when this does not vanish) by a factor of the order of the fine structure constant  $\alpha$ .

To obtain the complete expression for *magnetic dipole radiation*, the magnetic moment due to the electron *spin* must be added to the orbital magnetic moment.

The selection rules are found to be

$$\begin{aligned}\Delta l &= 0 \\ \Delta j &= 0, \pm 1 \\ \Delta m_j &= 0, \pm 1\end{aligned}\quad [4.107]$$

where  $j$  and  $m_j$  denote the quantum numbers associated respectively with the operators  $\mathbf{J}^2$  and  $J_z$ ,  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  being the total angular momentum of the electron. An example of magnetic dipole transition is that occurring between hyperfine levels of the ground state of atomic hydrogen at the wavelength of 21 cm, which we shall study in Chapter 5.

It is easy to see that the matrix elements of the products  $(xy)$ ,  $(yz)$  and  $(xz)$  vanish unless  $a$  and  $b$  are states of the same parity. The selection rules for *electric quadrupole radiation* are then given by

$$\begin{aligned}\Delta l &= 0, \pm 2 & (l = 0 \leftrightarrow l' = 0 \text{ forbidden}) \\ \Delta m &= 0, \pm 1, \pm 2\end{aligned}\quad [4.108]$$

We note that for  $\Delta l = \pm 2$  the contribution to  $M_{ba}$  is coming only from the electric quadrupole part, so that we have a pure electric quadrupole transition.

### Question 5

5. Prove the sum rule for the oscillator strength,  $\sum_k f_{ka} = 1$ .

### Answer

## Oscillator strengths and the Thomas–Reiche–Kuhn sum rule

In discussions of intensities it is customary to introduce a related dimensionless quantity  $f_{ka}$ , called the *oscillator strength*. It is defined as

$$f_{ka} = \frac{2m\omega_{ka}}{3\hbar} |\mathbf{r}_{ka}|^2 \quad [4.111]$$

with  $\omega_{ka} = (E_k - E_a)/\hbar$ . We note that this definition implies that  $f_{ka} > 0$  for absorption, where  $E_k > E_a$ . On the other hand we have  $f_{ka} < 0$  for emission processes.

The oscillator strengths [4.111] obey the sum rule, due to Thomas, Reiche and Kuhn

$$\sum_k f_{ka} = 1 \quad [4.112]$$

where the sum is over all levels, including the continuum. This sum rule can be proved as follows. Let  $f_{ka}^x$  be defined as

$$\begin{aligned} f_{ka}^x &= \frac{2m\omega_{ka}}{3\hbar} |x_{ka}|^2 \\ &= \frac{2m\omega_{ka}}{3\hbar} \langle a|x|k\rangle \langle k|x|a\rangle \end{aligned} \quad [4.113]$$

where we have used the simplified notation  $\langle a|x|k\rangle \equiv \langle \psi_a|x|\psi_k\rangle$ . From [4.59], we have

$$x_{ka} = \langle k|x|a\rangle = -\frac{i}{m\omega_{ka}} \langle k|p_x|a\rangle \quad [4.114a]$$

$$x_{ak} = \langle a|x|k\rangle = \frac{i}{m\omega_{ka}} \langle a|p_x|k\rangle \quad [4.114b]$$

and hence

$$f_{ka}^x = \frac{2i}{3\hbar} \langle a | p_x | k \rangle \langle k | x | a \rangle \quad [4.115a]$$

$$= -\frac{2i}{3\hbar} \langle a | x | k \rangle \langle k | p_x | a \rangle \quad [4.115b]$$

$$= \frac{i}{3\hbar} (\langle a | p_x | k \rangle \langle k | x | a \rangle - \langle a | x | k \rangle \langle k | p_x | a \rangle) \quad [4.115c]$$

where the last line has been obtained by taking half the sum of the two expressions [4.115a] and [4.115b].

We can now use the closure property of the hydrogenic wave functions which form a complete set, namely  $\sum_k |k\rangle\langle k| = 1$  to find from [4.115c] that

$$\sum_k f_{ka}^x = \frac{i}{3\hbar} \langle a | p_x x - x p_x | a \rangle \quad [4.116]$$

But since  $[x, p_x] = i\hbar$ , we have the sum rule

$$\sum_k f_{ka}^x = \frac{1}{3} \quad [4.117]$$

The same argument holds for  $f_{ka}^y$  and  $f_{ka}^z$ , which proves the sum rule [4.112].

### Question 6

6. Verify the identity:

$$\lim_{a \rightarrow 0} \frac{a}{x^2 + a^2} = \pi \delta(x)$$

### Answer (Tejas)

$$\begin{aligned}
 & x = a \tan \theta, \quad dx = a \sec^2 \theta d\theta \\
 \int_{-\infty}^{\infty} \frac{a}{x^2 + a^2} dx &= \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{a}{a^2 \sec^2 \theta} \times a \sec^2 \theta d\theta = \pi \quad \text{X} \quad \text{Z} \quad \text{Z} \quad \left( \text{O} \text{ C } \theta \right) \\
 \int_{-\infty}^{\infty} \frac{a}{x^2 + a^2} f(x) dx &= \int_{-\infty}^{\infty} \frac{a}{a^2(t^2+1)} f(at) \times a dt = \int_{-\infty}^{\infty} \frac{f(at)}{t^2+1} dt \\
 \left( t = \frac{x}{a} \Rightarrow x = at \right) \quad dx = adt & \quad \text{As } a \rightarrow 0, \quad f(at) \rightarrow f(0) \\
 \therefore \lim_{a \rightarrow 0} \int_{-\infty}^{\infty} \frac{f(at)}{t^2+1} dt &\rightarrow \int_{-\infty}^{\infty} \frac{f(0)}{t^2+1} dt = f(0) \int_{-\infty}^{\infty} \frac{dt}{t^2+1} = \pi f(0) \\
 \Rightarrow \lim_{a \rightarrow 0} \int_{-\infty}^{\infty} \frac{a}{x^2+a^2} f(x) dx &= \pi f(0) \quad \Rightarrow \boxed{\lim_{a \rightarrow 0} \frac{a}{x^2+a^2} = \pi f'(x)}
 \end{aligned}$$

## ▼ Section 5: Molecular Structure and Spectra

### Question 1