Problem Set 9 Answers
On the Hydrogen atom
and Matrix Representation of Operators and Eigenfunctions

1. (a) Average distance of the electron from the nucleus for H atom in the state function $\Psi_{1s} = \{1/\sqrt{\pi}\}\ \{Z/a_0\}^{3/2} \exp[-Zr/a_0]$ is given by
Use Postulate 3, the expectation value is
$\langle r\rangle = \iiint \Psi_{1s}{}^* \, r \, \Psi_{1s} \, r^2 dr \sin\theta d\theta d\phi =$
$\iiint\{1/\sqrt{\pi}\}\ \{Z/a_0\}^{3/2} \exp[-Zr/a_0]\ r\ \{1/\sqrt{\pi}\}\ \{Z/a_0\}^{3/2} \exp[-Zr/a_0]\ \ r^2 dr \sin\theta d\theta d\phi$
$\langle r\rangle = 4\pi(1/\pi)\ \{Z/a_0\}^3 \int r^3 \exp[-2Zr/a_0]dr$
This integral is of the form,
$\int_0^\infty x^n \exp(-ax)dx = n!/a^{n+1}$ for $a > 0$, n positive integer; here $n=3, a=2Z/a_0$
$\langle r\rangle = 4\pi(1/\pi)\ \{Z/a_0\}^3\ 3!(2Z/a_0)^{-4} = 4.3!(2)^{-4}(Z/a_0)^{-1} = (3/2)\ a_0$

(b) Probability for finding the electron at any one position is given by $\Psi^*\Psi$. The probability of finding the electron within a spherical shell between r and r+dr is given by $4\pi r^2\Psi_{1s}{}^*\ \Psi_{1s}$. To get maximum probability, need to find the distance at which the derivative of this probability is zero. First differentiate $4\pi r^2\ \Psi_{1s}{}^*\ \Psi_{1s}$, then set the derivative to zero, then solve for r.
Probability of finding the electron within a spherical shell, between r and r+ dr, is =
$\{(1/\pi)\ (Z/a_0)^3\ 4\pi r^2 \exp[-2Zr/a_0]\ dr.$
$d/dr\{\ 4\ (Z/a_0)^3\ r^2\exp[-2Zr/a_0]\ \} = 4\ (Z/a_0)^3 \exp[-2Zr/a_0][\ (-2Z/a_0)r^2 + 2r] = 0$
answer: $r=a_0/Z$

(c) Outcomes of measurements are the eigenvalues. The eigenvalues of the operator $L_z = (\hbar/i)\partial/\partial\varphi$ are given by $m = 0, \pm\hbar, \pm2\hbar, \ldots$ For the state whose function is $\Psi_{1s} = \{1/\sqrt{\pi}\}\ \{Z/a_0\}^{3/2} \exp[-Zr/a_0]$, m=0.
Therefore measurements of L_z on this state can yield only the eigenvalue 0.

(d) The average value of a series of measurements of L_z will be the average of a string of zeroes, which is zero.

(e) $\mathcal{H} = -(\hbar^2/2m)\nabla^2 - Ze^2/r$, $\quad L_z = (\hbar/i)\partial/\partial\varphi$
$\nabla^2 = \partial^2/\partial r^2 + (2/r)\ \partial/\partial r + \{r^2\sin\theta)^{-1}\partial/\partial\theta(\sin\theta\ \partial/\partial\theta) + r^2\sin^2\theta)^{-1}(\partial^2/\partial\phi^2)$
$\partial/\partial\varphi$ commutes with any terms in r or θ, and $\partial/\partial\varphi$ commutes with $(\partial^2/\partial\phi^2)$. Therefore, $[\mathcal{H}, L_z] = 0$
We have derived in lecture, $(d/dt)\ \langle S\rangle = (i/\hbar)\langle\mathbf{[}\ \mathcal{H}, L_z\mathbf{]}\ \rangle + (\partial/\partial t)\ S$
When $(d/dt)\ \langle S\rangle = 0$ then S is said to be a constant of the motion.
For $S = L_z$: $\quad (\partial/\partial t)\ (\hbar/i)\partial/\partial\varphi = 0$, no explicit t in the operator.
And we have already seen that $[\mathcal{H}, L_z] = 0$. Therefore, $(d/dt)\ \langle L_z\rangle = 0$; L_z is a constant of the motion.

2. Given $\Psi(r,\theta,\phi) = (1/81)(2/\pi)^{½} Z^{3/2} (6\text{-}Zr) Zr \exp[-Zr/3] \cos\theta$

(a) We can find n, ℓ, m just by inspection

n = 3 since the highest power in the polynomial in R(r) is given by n-1 and this has r^2.

ℓ = 1 since the $\Theta(\theta)$ part of the function has cos in the first power

m = 0 since the $\Phi(\phi)$ part of the H-like function is always $(2\pi)^{-½}\exp(im\phi)$ this one has a constant for the $\Phi(\phi)$ part

(b) The most probable value of r for an electron in the state specified by the $\Psi(r,\theta,\phi)$ given above, when Z = 1:

Probability for finding the electron at any one position is given by $\Psi^*\Psi$. The probability of finding the electron within a spherical shell between r and r+dr is given by $\iint \cos^2\theta \sin\theta d\phi\ r^2\Psi_{310}{}^* \Psi_{310}\ dr$. The integral $\iint \cos^2\theta\sin\theta d\phi = 2\pi$. To get maximum probability, need to find the distance at which the derivative of this probability is zero. First differentiate $2\pi r^2 \Psi_{310}{}^* \Psi_{310}$, then set the derivative to zero, then solve for r.

For Z=1, the probability of finding the electron within a spherical shell, between r and r+ dr, is = $2\pi r^2 (1/81)^2(2/\pi) (6\text{-}r)^2 r^2 \exp[-2r/3]$ dr.

Differentiating,

$d/dr\{2\pi(1/81)^2(2/\pi) (6\text{-}r)^2 r^4\exp[-2r/3]\}$ =? We do not need the constants to find r that makes the derivative go to zero:

$d/dr\{ (6\text{-}r)^2 r^4\exp[-2r/3]\} = \{-(2/3) (6\text{-}r)^2 r^4 \}\exp[-2r/3] + \exp[-2r/3] \{36x4r^3\text{-}12x5r^4+6r^5\}$
$=0 = \{-2/3(36\text{-}12r+r^2)r^4 + 36x4r^3\text{-}12x5r^4+6r^5\}=0$

Factor out r^3 : $\{-2/3(36\text{-}12r+r^2)r+ 36x4 \text{-}12x5r+ 6r^2\}=0$

$\{144\text{-}84r +14r^2\text{-}(2/3)r^3\} =0$ answer: r = 3 . The most probable value for r for the electron is $3a_0$

<u>Easier way</u>: $r^2 \Psi_{310}{}^* \Psi_{310}$ is maximum when $r\Psi_{310}$ is maximum. Easier to do $d/dr\{r(6\text{-}r)r \exp[-r/3]\}$, again using Z=1 and ignoring the constants we get:

$-(1/3)(6r^2\text{-}r^3)+(12r\text{-}3r^2) =0$ leaving out $\exp[-r/3]$. Now factor out r too, we get $36\text{-}15r+r^2=0$, $(r\text{-}12)(r\text{-}3)=0$ from which we get r=3 or r=12.

(c) The function with the same n and ℓ and m +1 is Ψ_{311}. Since m=0 has the function $\Phi_0(\phi)=(2\pi)^{-½}$ and we want $\Phi_1(\phi)=(2\pi)^{-½}\exp(i\phi)$ However, we also need to change the $\Theta_{\ell m}(\theta)$ since this also depends on |m|. To get the proper function we need to use the raising operator which will take our angular momentum function from $Y_{10}(\theta,\phi)$ to $Y_{11}(\theta,\phi)$. One form of the raising operator is

$$(L_x + iL_y) = e^{i\phi}\, \partial/\partial\theta + i\, e^{i\phi} \cdot\cot\theta\cdot\partial/\partial\phi$$

The second term vanishes because the original function $\Psi(r,\theta,\phi) = (1/81)(2/\pi)^{½} Z^{3/2} (6\text{-}Zr) Zr \exp[-Zr/3] \cos\theta$ has no explicit ϕ

Applying the first term $\exp^{i\phi}\partial/\partial\theta \cos\theta$ gives $\exp^{i\phi} \sin\theta$

$\Psi_{311}(r,\theta,\phi) \propto Z^{3/2}\,(6-Zr)\,Zr\,\exp[-Zr/3]\,\sin\theta\,\exp(i\phi)$

(d) The hamiltonian for a hydrogen-like atom (only the internal motion of the electron relative to the nucleus)

$\nabla^2 = (1/r^2)\{\partial/\partial r\,(r^2\partial/\partial r)\ -\ L^2\}$

$\mathcal{H} = -\hbar^2/2\mu\ \ \{(1/r^2)[\partial/\partial r\,(r^2\partial/\partial r)\ -\ L^2]\ -Ze^2/r$

(e) It is possible to determine simultaneously the energy of a hydrogen atom and its angular momentum because $[\mathcal{H}, L^2] = 0$ and $[\mathcal{H}, L_z] = 0$. We see this by inspection: $[\mathcal{H}, L^2] = [-\hbar^2/2\mu\,(1/r^2)\{\partial/\partial r\,(r^2\partial/\partial r)\}\ -Ze^2/r,\ L^2] = 0$, since L^2 is only a function of θ and φ and not a function of r, the two operators are in different independent variables and therefore the order of the operations is irrelevant. And of course L^2 commutes with itself. By the same reasoning, $[-\hbar^2/2\mu\,(1/r^2)\{\partial/\partial r\,(r^2\partial/\partial r)\}\ -Ze^2/r,\ L_z] = 0$ since L_z operator is in terms of φ only, and we already know from properties of any angular momentum that L_z commutes with L^2.

3. (a) Transition probability is proportional to the square of the integral

$$M = \iiint \Psi_{n\ell m}^{*}\ x\ \Psi_{n'\ell'm'}\ r^2 dr \sin\theta d\theta d\phi$$

using $x = r\sin\theta\cos\phi = r\sin\theta\,[\exp^{i\phi} + \exp^{-i\phi}]/2$

$$M = \iiint R(r)_{n\ell}\Theta_{\ell m}\,(2\pi)^{-1/2}\exp^{-im\phi}\ r\sin\theta\,[\exp^{i\phi} + \exp^{-i\phi}]/2\ R(r)_{n'\ell'}\Theta_{\ell'm'}\,(2\pi)^{-1/2}\exp^{im'\phi}\ r^2 dr\sin\theta d\theta d\phi$$

Integration over r part does not vanish.

Integration over the φ part: $\int \exp^{-im\phi}\,[\exp^{i\phi} + \exp^{-i\phi}]\,\exp^{im'\phi}\,d\phi$ gives $\int \exp^{(-im+i+im')\phi}\,d\phi + \int \exp^{(-im-i+im')\phi}\,d\phi$. The first integral vanishes unless $-m+1+m' = 0$, that is $m'-m = -1$. The second integral vanishes unless $-m-1+m' = 0$, that is $m'-m = +1$.

Integration over the θ part: $\int \Theta_{\ell m}\sin\theta\,\Theta_{\ell'm'}\sin\theta d\theta$. We can make use of the relation:

$$\cos\theta\,Y_{\ell m} = \{(\ell^2 - m^2)/[(2\ell-1)(2\ell+1)]\}^{1/2}\,Y_{\ell-1,m} + \{[(\ell+1)^2 - m^2]/[(2\ell+1)(2\ell+3)]\}^{1/2}\,Y_{\ell+1,m}$$

There is a similar relation for $\sin\theta\,Y_{\ell m}$: $\sin\theta\,Y_{\ell m} = \sim\sim Y_{\ell-1,m} + \sim\sim Y_{\ell+1,m}$

$$\int\Theta_{\ell m}\sin\theta\,\Theta_{\ell'm'}\sin\theta d\theta = \sim\sim\int\Theta_{\ell m}\,\Theta_{\ell'-1m'}\sin\theta d\theta + \sim\sim\int\Theta_{\ell m}\,\Theta_{\ell'+1m'}\sin\theta d\theta$$

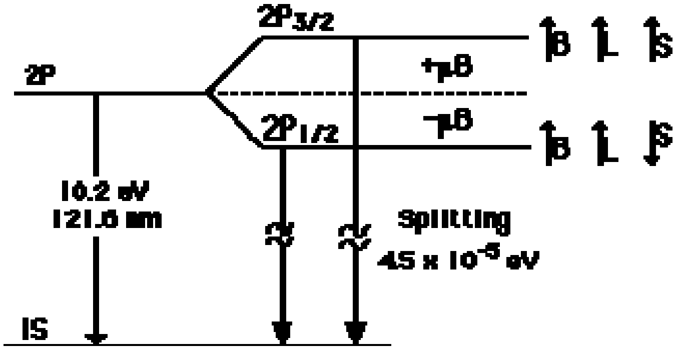
Because of orthonormality of the $\Theta_{\ell m}$ functions, the integrals vanish unless $\ell = \ell'-1$ or $\ell = \ell'+1$, that is, $\ell - \ell' = \pm 1$

In summary, the selection rules of atomic spectroscopy are: $m-m' = \pm 1$ and $\ell - \ell' = \pm 1$.

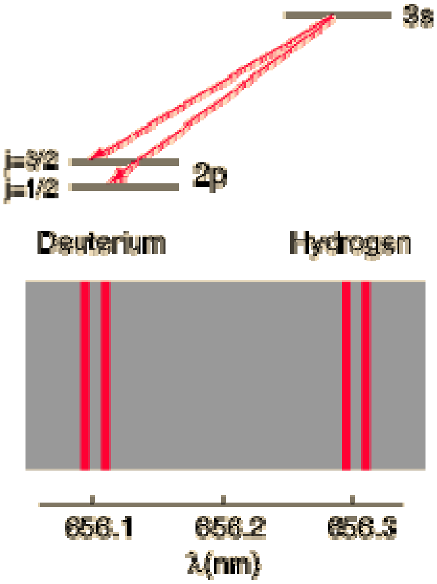
There is also $\iiint \Psi_{n\ell m}{}^{*}\, z\, \Psi_{n'\ell'm'}\, r^2 dr \sin\theta\, d\theta\, d\phi$ using $z = r\cos\theta$ we will get $m-m'=0$ and $\ell - \ell' = \pm1$ for light polarized in the z direction.

(b) The displacement of the deuterium wavelength from the hydrogen wavelength for the first Balmer line. The first Balmer line corresponds to the transition n=2 to n=3.
see http://hyperphysics.phy-astr.gsu.edu/HBASE/quantum/hydfin.html#c1

When the spectral lines of the hydrogen spectrum are examined at very high resolution, they are found to be closely-spaced doublets. This splitting is called fine structure and was one of the first experimental evidences for electron spin.



The small splitting of the spectral line is attributed to an interaction between the electron spin S and the orbital angular momentum L. It is called the spin-orbit interaction.



The familiar red H-alpha line of hydrogen is a single line according to the Bohr theory. The straight application of the Schrodinger equation to the hydrogen atom gives the same result. If you calculate the wavelength of this line using the energy expression from the Bohr theory, you get 656.11 nm for hydrogen, treating the nucleus as a fixed center. If you use the reduced mass, you get 656.47 nm for hydrogen and 656.29 nm for deuterium. The difference between the hydrogen and deuterium lines is about 0.2 nm and the splitting of each of them is about 0.016 nm, corresponding to an energy difference of about 0.000045 eV. This corresponds to an internal magnetic field on the electron of about 0.4 Tesla.

The reduced mass μ which appears in the motion of the electron relative to the nucleus after the separation of the center of mass motion (translation) is given by

$1/\mu = 1/m_e + 1/m_N$

$\mathcal{H} = -\hbar^2/2\mu \ \{(1/r^2)[\partial/\partial r\ (r^2\partial/\partial r)\ -\ L^2]\ -Ze^2/r$

The energies of the hydrogen atom are given by $-(Z^2/n^2)(e^2/2a)$ where $a = \hbar^2/\mu e^2$ or $a = 4\pi\varepsilon 0\hbar^2/\mu e^2$

For the transition n=2 to 3 the energy difference is $-\ (e^2/2a)[1/2^2\ -1/3^2] =$ and the wavelength corresponding to this energy difference is hc/λ

$\lambda = (2a/hce^2)(36/5) = 2(36/5)(\hbar^2/\mu e^2)/hce^2 = 2(36/5)(h/4\pi^2)/\mu ce^4$

Taking the ratio of two such equations, one for D atom the other for H atom:

$m_p = 1.672\ 621\ 637(83) \times 10^{-24}$ g $m_d = 3.343\ 583\ 20(17) \times 10^{-24}$ g

$m_e = 9.109\ 382\ 15(45) \times 10^{-28}$ g

$\lambda_D/\lambda_H = \mu_H/\mu_D = 0.9997$ so the isotope shift is very small.

The difference between the H and the D atom Balmer line wavelengths would be given by $\Delta\lambda = \{2(36/5)(h/4\pi^2)/\ ce^4\}(1/\mu_H\ -1/\mu_D) = \lambda_H\ \mu_H(1/\mu_H\ -1/\mu_D)$

where $(1/\mu_H\ -1/\mu_D) = 1/m_e+1/m_p\ -\ 1/m_e-1/m_d = 1/m_p\ -1/m_d\ = (m_d-m_p)/(m_pm_d)$

$\Delta\lambda = \ \lambda_H\ \mu_H\ (1/m_p\ -1/m_d) = \ \lambda_H\ m_e\ (m_d-m_p)/(m_pm_d)]$

$\Delta\lambda = \ \lambda_H\ 2.7217 \times 10^{-4}$

on Matrix Representation of Operators and Wavefunctions

Using the eigenfunctions of S_z as a complete set of basis functions, (we found these in Problem Set 8):

$\psi_1 = \varphi_{\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$

$\psi_{0a} = \varphi_{\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$

$\psi_{0b} = \varphi_{-\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$

$\psi_{-1} = \varphi_{-\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$

the matrix representation of

$\mathbf{S}(1)\bullet\mathbf{S}(2) = \{\ \frac{1}{2}S_+(1)S_-(2)\ +\ \frac{1}{2}\ S_-(1)S_+(2)\ + S_z(1)\ S_z(2)\ \}$

	$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$	$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$
$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	$(\frac{1}{2})^2\hbar^2$	0	0	0
$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$	0	$-(\frac{1}{2})^2\hbar^2$	$(\frac{1}{2})\hbar^2$	0
$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	0	$(\frac{1}{2})\hbar^2$	$-(\frac{1}{2})^2\hbar^2$	0
$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$	0	0	0	$(-\frac{1}{2})^2\hbar^2$

the matrix representation of $\mathbf{S}^2$: From Problem 8 we found:

$\mathbf{S}^2 = \mathbf{S}(1)^2 + 2\,\mathbf{S}(1)\bullet\mathbf{S}(2) + \mathbf{S}(2)^2 = \frac{1}{2}\,\mathcal{S}_+(1)\,\mathcal{S}_-(1) + \frac{1}{2}\,\mathcal{S}_-(1)\,\mathcal{S}_+(1) + S_z(1)^2$

$+ \frac{1}{2}\,\mathcal{S}_+(2)\,\mathcal{S}_-(2) + \frac{1}{2}\,\mathcal{S}_-(2)\,\mathcal{S}_+(2) + S_z(2)^2 + \{\mathcal{S}_+(1)\mathcal{S}_-(2) + \mathcal{S}_-(1)\mathcal{S}_+(2) + 2S_z(1)S_z(2)\}$

	$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$	$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$
$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	$2\hbar^2$	0	0	0
$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$	0	$\hbar^2$	$\hbar^2$	0
$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	0	$\hbar^2$	$\hbar^2$	0
$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$	0	0	0	$2\hbar^2$

the matrix representation of

$\mathcal{H}_{\text{op}} = a_1S_z(1) + a_2S_z(2) + J\mathbf{S}(1)\bullet\mathbf{S}(2)$

	$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$	$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$
$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	$a_1(\frac{1}{2})\hbar$ $+ a_2(\frac{1}{2})\hbar$ $+J(\frac{1}{2})^2\hbar^2$	0	0	0
$\varphi_{\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$	0	$a_1(\frac{1}{2})\hbar$ $- a_2(\frac{1}{2})\hbar$ $-J(\frac{1}{2})^2\hbar^2$	$J(\frac{1}{2})\hbar^2$	0
$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{\frac{1}{2}}(2)$	0	$J(\frac{1}{2})\hbar^2$	$- a_1(\frac{1}{2})\hbar$ $+ a_2(\frac{1}{2})\hbar$ $-J(\frac{1}{2})^2\hbar^2$	0
$\varphi_{-\frac{1}{2}}(1)\bullet\varphi_{-\frac{1}{2}}(2)$	0	0	0	$- a_1(\frac{1}{2})\hbar$ $- a_2(\frac{1}{2})\hbar$ $J(-\frac{1}{2})^2\hbar^2$

for $a_1 = 2/\hbar$, $a_2 = 2/\hbar$, $J = 4/\hbar^2$

	$\varphi_{½}(1)\bullet\varphi_{½}(2)$	$\varphi_{½}(1)\bullet\varphi_{-½}(2)$	$\varphi_{-½}(1)\bullet\varphi_{½}(2)$	$\varphi_{-½}(1)\bullet\varphi_{-½}(2)$
$\varphi_{½}(1)\bullet\varphi_{½}(2)$	1 + 1 +1	0	0	0
$\varphi_{½}(1)\bullet\varphi_{-½}(2)$	0	1 - 1 -1	1	0
$\varphi_{-½}(1)\bullet\varphi_{½}(2)$	0	1	- 1 + 1 -1	0
$\varphi_{-½}(1)\bullet\varphi_{-½}(2)$	0	0	0	- 1 - 1 +1

The solutions are (see problem below for more detailed solution of a similar matrix):

$E_1 = 3$ $\Psi_1(1,2) = \varphi_{½}(1)\bullet\varphi_{½}(2)$ by inspection

$E_4 = -1$ $\Psi_4(1,2) = \varphi_{-½}(1)\bullet\varphi_{-½}(2)$ by inspection

$$\det \begin{array}{|c|c|} \hline -1-E & 1 \\ \hline 1 & -1-E \\ \hline \end{array} = 0$$

Evaluating the determinant, $(-1-E)^2 -1 =0$

The roots are $E = 0$, or -2

For $E = 0$: $(-1-0)C_a +1C_b = 0$ $C_a = C_b$, normalization gives

$\Psi_2(1,2) = (1/\sqrt{2})\, \varphi_{½}(1)\bullet\varphi_{-½}(2) + (1/\sqrt{2})\, \varphi_{-½}(1)\bullet\varphi_{½}(2)$

For $E = -2$: $(-1+2)C_a +1C_b = 0$ $C_a = - C_b$, normalization gives

$\Psi_3(1,2) = (1/\sqrt{2})\, \varphi_{½}(1)\bullet\varphi_{-½}(2) - (1/\sqrt{2})\, \varphi_{-½}(1)\bullet\varphi_{½}(2)$

Energy level diagram:

3 ------$\Psi_1(1,2) = \varphi_{½}(1)\bullet\varphi_{½}(2)$

0 ------$\Psi_2(1,2) = (1/\sqrt{2})\, \varphi_{½}(1)\bullet\varphi_{-½}(2) + (1/\sqrt{2})\, \varphi_{-½}(1)\bullet\varphi_{½}(2)$
-1 ------$\Psi_4(1,2) = \varphi_{-½}(1)\bullet\varphi_{-½}(2)$
-2 ------$\Psi_3(1,2) = (1/\sqrt{2})\, \varphi_{½}(1)\bullet\varphi_{-½}(2) - (1/\sqrt{2})\, \varphi_{-½}(1)\bullet\varphi_{½}(2)$

2. T**o** find the simultaneous eigenfunctions of the operators

$$F_z \equiv I_z(1) + I_z(2) \quad \text{and} \quad F^2 \equiv F_x^2 + F_y^2 + F_z^2$$

Given

$I_z(1)\alpha(1) = \frac{1}{2}\hbar\,\alpha(1)$ $\qquad$ $I_z(1)\,\beta(1) = -\frac{1}{2}\hbar\,\beta(1)$

$I_x(1)\alpha(1) = \frac{1}{2}\hbar\,\beta(1)$ $\qquad$ $I_x(1)\,\beta(1) = \frac{1}{2}\hbar\,\alpha(1)$

$I_y(1)\alpha(1) = \frac{1}{2}i\hbar\,\beta(1)$ $\qquad$ $I_y(1)\,\beta(1) = -\frac{1}{2}i\hbar\,\alpha(1)$

We start with a complete orthonormal set of eigenfunctions of F_z using separation of variables: Since F_z is a sum of two operators, the eigenfunctions of F_z can be written as products of the eigenfunctions of each of the operators $I_z(1)$ and $I_z(2)$ and the eigenvalues can be obtained by operating on the functions

	eigenfunctions of F_z	eigenvalue of F_z
ψ_1	$\alpha(1)\bullet\alpha(2)$	$\hbar$
ψ_2	$\alpha(1)\bullet\beta(2)$	0
ψ_3	$\beta(1)\bullet\alpha(2)$	0
ψ_4	$\beta(1)\bullet\beta(2)$	$-\hbar$

$\mathbf{F}^2 \equiv F_x^2 + F_y^2 + F_z^2$

We could just find the matrix representation of $\mathbf{F}^2$ in this complete orthonormal set and then find the eigenvalues and eigenfunctions of the matrix.

$\mathbf{F}^2 = \mathbf{I}(1)^2 + 2\,\mathbf{I}(1)\bullet\mathbf{I}(2) + \mathbf{I}(2)^2 = \frac{1}{2} I_+(1)\, I_-(1) + \frac{1}{2} I_-(1)\, I_+(1) + I_z(1)^2$
$+ \frac{1}{2} I_+(2)\, I_-(2) + \frac{1}{2} I_-(2)\, I_+(2) + I_z(2)^2 + \{I_+(1)I_-(2) + I_-(1)I_+(2) + 2I_z(1)I_z(2)\}$ (this identity derived for another angular momentum in Problem Set 8)

The matrix representation of $\mathbf{F}^2$ is

	$\alpha(1)\bullet\alpha(2)$	$\alpha(1)\bullet\beta(2)$	$\beta(1)\bullet\alpha(2)$	$\beta(1)\bullet\beta(2)$
$\alpha(1)\bullet\alpha(2)$	$2\hbar^2$	0	0	0
$\alpha(1)\bullet\beta(2)$	0	$\hbar^2$	$\hbar^2$	0
$\beta(1)\bullet\alpha(2)$	0	$\hbar^2$	$\hbar^2$	0
$\beta(1)\bullet\beta(2)$	0	0	0	$2\hbar^2$

Matrix diagonalization of the matrix above will give both the eigenvalues and the eigenfunctions of $\mathbf{F}^2$. We solve the matrix equation $\mathbf{F}^2\mathbf{C} = \mathbf{C}\mathbf{f}$ where f are the eigenvalues. When this matrix multiplication is carried out the matrix equation is written out as simultaneous equations to be solved,

$F_{11}\,C_1 + F_{12}C_2 + F_{13}C_3 + F_{14}C_4 = fC_1$
$F_{21}\,C_1 + F_{22}C_2 + F_{23}C_3 + F_{24}C_4 = fC_2$
$F_{31}\,C_1 + F_{32}C_2 + F_{33}C_3 + F_{34}C_4 = fC_3$
$F_{41}\,C_1 + F_{42}C_2 + F_{43}C_3 + F_{44}C_4 = fC_4$

The linear equations will have a non-trivial solution if and only if the determinant of the coefficients vanishes.

$$\det \begin{vmatrix} F_{11} - f & F_{12} & F_{13} & F_{14} \\ F_{21} & F_{22} - f & F_{23} & F_{24} \\ F_{31} & F_{32} & F_{33} - f & F_{34} \\ F_{41} & F_{42} & F_{43} & F_{44} - f \end{vmatrix} =0$$

The integrals which constitute the matrix elements are eva;uated:

$$\det \begin{vmatrix} 2\hbar^2 - f & 0 & 0 & 0 \\ 0 & \hbar^2 - f & \hbar^2 & 0 \\ 0 & \hbar^2 & \hbar^2 - f & 0 \\ 0 & 0 & 0 & 2\hbar^2 - f \end{vmatrix} =0$$

ψ_1 does not mix with any other function and is therefore an eigenfunction of $\mathbf{F}^2$ because, as we can see, when F^2 operates on this function, only the same function results and no others. Also ψ_4 does not mix with any other function, and is therefore an eigenfunction of $\mathbf{F}^2$.

Now evaluating the 2x2 determinant, setting it to zero :

$$\begin{vmatrix} \hbar^2 - f & \hbar^2 \\ \hbar^2 & \hbar^2 - f \end{vmatrix}$$

$(\hbar^2 - f)^2 - \hbar^4 = 0$ leads to $\pm(\hbar^2 - f) = \hbar^2$ or $f = 0, 2\hbar^2$

Substituting $f = 2\hbar^2$ leads to $-\hbar^2 C_2 + \hbar^2 C_3 = 0$, which means $C_2 = C_3$

Normalization gives $\Psi_2 = [\alpha(1) \bullet \beta(2) + \beta(1) \bullet \alpha(2)]/\sqrt{2}$

Substituting $f = 0$ leads to $\hbar^2 C_2 + \hbar^2 C_3 = 0$, which means $C_2 = -C_3$

Normalization gives gives $\Psi_3 = [\alpha(1) \bullet \beta(2) - \beta(1) \bullet \alpha(2)]/\sqrt{2}$

Simultaneous eigenfunctions of $\mathbf{F}^2$ and $\mathbf{F}_z$	eigenvalues f	eigenvalues of F_z
$\Psi_1 = \alpha(1) \bullet \alpha(2)$	$2\hbar^2$	$\hbar$
$\Psi_2 = [\alpha(1) \bullet \beta(2) + \beta(1) \bullet \alpha(2)]/\sqrt{2}$	$2\hbar^2$	0
$\Psi_3 = [\alpha(1) \bullet \beta(2) - \beta(1) \bullet \alpha(2)]/\sqrt{2}$	0	0
$\Psi_4 = \beta(1) \bullet \beta(2)$	$2\hbar^2$	$-\hbar$

We could have also used the properties of commuting operators:

Since I is an angular momentum operator, then F is an angular momentum operator, thus, $[F_z, F^2] = 0$. Since these operators commute, they have the same set of eigenfunctions, except that any linear combination of the degenerate eigenfunctions of one operator F_z are also eigenfunctions of F_z, so that the specific linear combination that is an eigenfunction of F^2 has to be found.

From the above table, $\Psi_1 = \alpha(1) \bullet \alpha(2)$ is an eigenfunction of F^2

$\Psi_4 = \beta(1) \bullet \beta(2)$ is an eigenfunction of F^2

Now we need to find the linear combination of $\psi_2 = \alpha(1) \bullet \beta(2)$ and $\psi_3 = \beta(1) \bullet \alpha(2)$ to make Ψ_2 and Ψ_3 that are eigenfunctions of F^2. Etc.