# Physics 531 - Atom/Molecular Physics

## Problem Set #1 Solutions

**Problem 1**: The variational method

(a) 1D SHO. Take Gaussian trial wave function

$$\psi_\alpha(x) = e^{-\alpha x^2}$$

Mean energy $\bar{H}_\alpha = \dfrac{\langle\psi_\alpha|\hat{H}|\psi_\alpha\rangle}{\langle\psi_\alpha|\psi_\alpha\rangle}$ $\qquad \hat{H} = \dfrac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$

$$\langle\psi_\alpha|\psi_\alpha\rangle = \int_{-\infty}^{\infty} dx\, e^{-2\alpha x^2} = \sqrt{\frac{\pi}{2\alpha}}$$

$$\langle\psi_\alpha|\hat{H}|\psi_\alpha\rangle = \frac{\hbar^2}{2m}\sqrt{\frac{\pi\alpha}{2}} + \frac{1}{8}m\omega^2\sqrt{\frac{\pi}{2}}$$

$$\int_{-\infty}^{\infty} dx\, \psi_\alpha(x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2\right)\psi(x)$$

$$\Rightarrow \bar{H}_\alpha = \frac{\hbar^2}{2m}\alpha + \frac{1}{8}m\omega^2\frac{1}{\alpha}$$

$$\frac{d\bar{H}_\alpha}{d\alpha} = 0 \Rightarrow \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0 \Rightarrow \alpha_{min} = \frac{m\omega}{2\hbar}$$

$$\Rightarrow \boxed{\psi_{\alpha_{min}}(x) = \sqrt{\frac{m\omega}{\pi\hbar}}\, e^{-\frac{m\omega x^2}{2\hbar}}}$$

$$\boxed{\bar{H}_{\alpha_{min}} = \frac{\hbar\omega}{2}}$$

Correct ground state.

Moral: If, by chance you choose the exact form of the trial ground state, minimization of the mean will lead to the exact solution.

(b) Suppose we choose the trial $\psi_\alpha = \frac{1}{x^2+\alpha}$

$$\langle \psi_\alpha | \psi_\alpha \rangle = \frac{\pi}{2\sqrt{\alpha^3}}$$

$$\langle \psi_\alpha | \hat{H} | \psi_\alpha \rangle = \frac{1}{\sqrt{\alpha^5}} \pi \left( \frac{\hbar^2}{8m} + \frac{1}{4} m\omega^2 \alpha^2 \right)$$

$$\Rightarrow \bar{H}_\alpha = \frac{\hbar^2}{4\alpha m} + \frac{1}{2} m\omega^2 \alpha$$

$$\frac{d\bar{H}_\alpha}{d\alpha} = 0 \Rightarrow \alpha_{min} = \frac{\hbar}{\sqrt{2} m\omega}$$

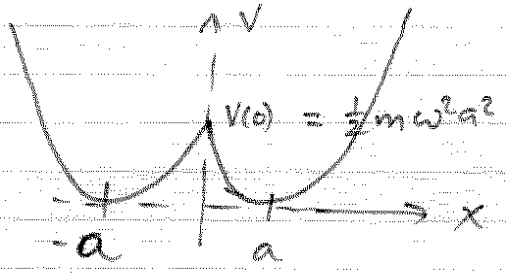
$$\therefore \boxed{\bar{H}_{\alpha min} = \frac{1}{\sqrt{2}} \hbar\omega}$$

Not bad 20% of $\hbar\omega$ off from exact answer

Though the variational method can give reasonably close answers for the ground state energy, it is not a "controlled" approximation, i.e., there is no small parameter with which we can know the accuracy of the result.

(c) Double Oscillator $V(x) = \frac{1}{2} m\omega^2 (|x| - a)^2$

From Merzbacher Chap 8.5




Trial wave functions: Since $V(x)$ is invariant under reflection, the eigenstates have good parity (sym or antisym)

$\Rightarrow$ Choose $\psi_n^{(\pm)}(x) = u_n(x-a) \pm u_n(x+a)$

where $u_n(x)$ = Harmonic oscillator wave fnct
Hermite polynomial × Gaussian

(d) The variational estimate is the mean value since we have no parameter to minimize

$$\Rightarrow E_n^{(\pm)} = \frac{\langle \psi_n^{(\pm)} | \hat{H} | \psi_n^{(\pm)} \rangle}{\langle \psi_n^{(\pm)} | \psi_n^{(\pm)} \rangle}$$

- $\langle \psi_n^{(\pm)} | \psi_n^{(\pm)} \rangle = \underbrace{\langle u_n^{(+)} | u_n^{(+)} \rangle}_{1} + \underbrace{\langle u_n^{(-)} | u_n^{(-)} \rangle}_{1} \pm 2 \underbrace{\langle u_n^{(+)} | u_n^{(-)} \rangle}_{C_n}$

where $u_n^{(\pm)}(x) = u_n(x \mp a) = \langle x | u_n^{(\pm)} \rangle$

- $\langle \psi_n^{(\pm)} | \hat{H} | \psi_n^{(\pm)} \rangle = \langle u_n^{(+)} | \hat{H} | u_n^{(+)} \rangle + \langle u_n^{(-)} | \hat{H} | u_n^{(-)} \rangle$
$\pm \langle u_n^{(+)} | \hat{H} | u_n^{(-)} \rangle \pm \langle u_n^{(-)} | \hat{H} | u_n^{(+)} \rangle$
$= 2(A_n \pm B_n)$ (by parity)

$$\Rightarrow \boxed{E_n^{(\pm)} = \frac{A_n \pm B_n}{1 + C_n}}$$

$A_n, B_n, C_n$ given in assignment

(e) For ground state $\left( u_0(x) = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} \right.$
$\left.$ where $\beta \equiv \frac{m\omega}{\hbar} \right)$

Ground state splitting $\Delta E_0 = E_0^{(-)} - E_0^{(+)}$

$$\Rightarrow \Delta E_0 = \frac{-2B_0}{1 + C_0}$$

$$C_0 = \int_{-\infty}^{\infty} dx\; u_0(x+a)\, u_0(x-a) = \sqrt{\frac{\beta}{\pi}} \int_{-\infty}^{\infty} e^{-\beta/2\,[(x+a)^2 + (x-a)^2]}$$

$$= e^{-\beta a^2} \underbrace{\sqrt{\frac{\beta}{\pi}} \int_{-\infty}^{\infty} e^{-\beta x^2}}_{=1} = e^{-\beta a^2}$$

$$B_0 = \int_{-\infty}^{\infty} dx\; u_0(x+a)\, \hat{H}\, u_0(x-a) = \int_{-\infty}^{0} dx\; u_0(x+a)\, \hat{H}_-\, u_0(x+a)$$

where $\left(\hat{H}_\pm = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2(x \mp a)^2\right)$ $\quad + \int_{0}^{\infty} dx\; u_0(x+a)\, \hat{H}_+\, u_0(x-a)$

Note $\hat{H}_\pm\, u_0(x \mp a) = \frac{\hbar\omega}{2}\, u_0(x \mp a)$ (Eigenvalue $E_0$.)

Aside: $\int_{-\infty}^{0} dx\; u_0(x+a)\, \hat{H}_-\, u_0(x-a) = \int_{-\infty}^{0} dx \left(\hat{H}_- u_0(x+a)\right) u_0(x-a)$

Using integration by parts $\quad -\frac{\hbar^2}{2m}\left[\frac{du_-}{dx}\, u_+(x) - u_-(x)\, \frac{du_+}{dx}\right]$

$$\Rightarrow B_0 = \frac{\hbar\omega}{2}\left(1 - 2\sqrt{\frac{\beta}{\pi}}\, a\right) e^{-\beta a^2}$$

$$\Rightarrow \Delta E_0 = -2\,\frac{\hbar\omega}{2}\left(1 - 2\sqrt{\frac{\beta}{\pi}}\, a\right) \frac{e^{-\beta a^2}}{1 + e^{-\beta a^2}}$$

For $a \gg \sqrt{\frac{\hbar}{m\omega}}$ $\Rightarrow$ $\Delta E_0 = 2\hbar\omega \sqrt{\frac{\beta a^2}{\pi}}\, e^{-\beta a^2}$

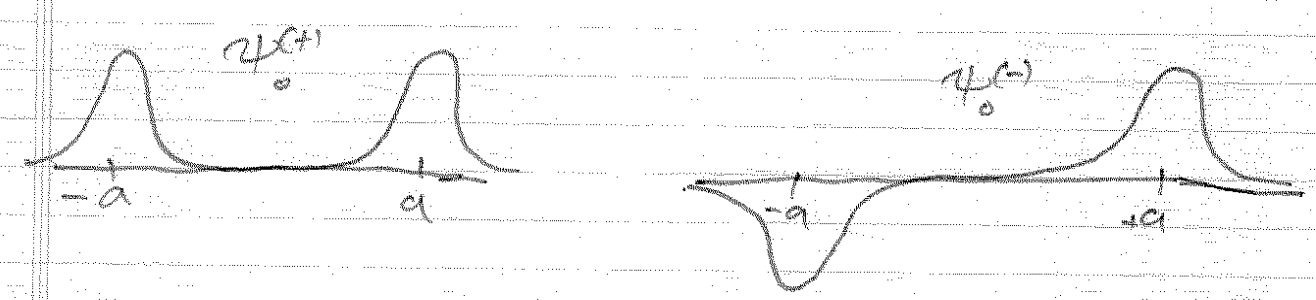
Note $\beta a^2 = \frac{m\omega a^2}{\hbar} = \frac{2V_0}{\hbar\omega}$ $\Rightarrow$ $\boxed{\Delta E_0 = 2\hbar\omega \sqrt{\frac{2V_0}{\hbar\omega}}\, e^{-\frac{2V_0}{\hbar\omega}}}$

This is known as the "tunneling splitting" since the energy difference determines the frequency of tunnelling between the left/right wells $\boxed{\omega_{tunnel} = \frac{\Delta E_0}{\hbar}}$

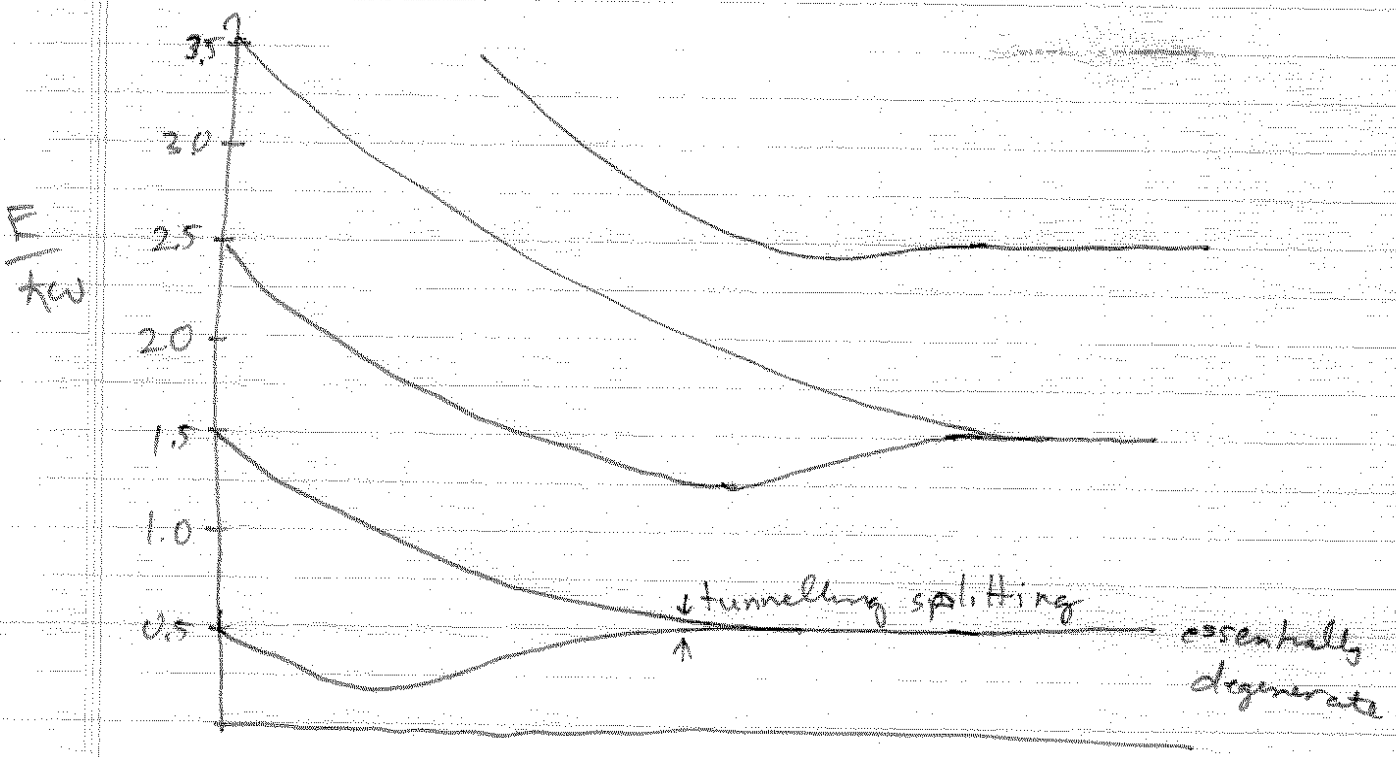
(f) When $a \gg \sqrt{\frac{\hbar}{m\omega}}$ we have tunneling splitting.

When $a \to 0$ we have a single oscillator: $\hbar\omega(n+\frac{1}{2})$

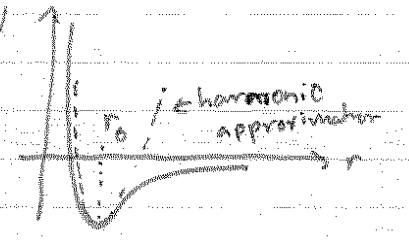
Ground doublet:




- The symmetric state must match on to the ground state of the single oscillator
- The antisymmetric state must match on to first excited state



## Problem 2: Lennard-Jones Potential




$$V(r) = \underbrace{\frac{C_{12}}{r^{12}}}_{\text{short-range repulsive}} - \underbrace{\frac{C_6}{r^6}}_{\text{long-range attractive van der Waals}}$$

(a) The equilibrium point $r_0$: $\left.\frac{dV}{dr}\right|_{r_0} = 0 \Rightarrow r_0 = \left(\frac{2C_{12}}{C_6}\right)^{1/6}$

$$\frac{-12C_{12}}{r_0^{13}} + \frac{6C_6}{r^7}$$

Expand in Taylor Series

$$V(r) = V(r_0) + \cancel{\left.\frac{dV}{dr}\right|_{r_0}}^{0}(r-r_0) + \frac{1}{2}\left.\frac{d^2V}{dr^2}\right|_{r_0}(r-r_0)^2 + \frac{1}{3!}\left.\frac{d^3V}{dr^3}\right|_{r_0}(r-r_0)^3 + \dots$$

$$= \underbrace{V_0}_{\text{constant}} + \underbrace{\frac{1}{2}V_0''(r-r_0)^2}_{\frac{1}{2}m\omega^2x^2} + \frac{1}{6}V_0'''(r-r_0)^3 + \dots$$

$$\xi x^3 + \dots$$

where $m\omega^2 = V_0''$ $\quad \xi = \frac{V_0'''}{6}$ $\quad x = r - r_0$ (displacement)

$$\Rightarrow \hat{H} = \hat{H}_0 + \hat{H}_1 \quad \text{where} \quad \hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \qquad \hat{H}_1 = \xi\hat{x}^3$$

(b) To find the small parameter we seek the characteristic scales.

For $\hat{H}_0 \Rightarrow E_0 = \hbar\omega$

For $\hat{H}_1 \Rightarrow E_1 = \xi x_0^3$ where $x_0 = \sqrt{\frac{\hbar}{m\omega}}$ = characteristic width of wavepacket

$$\Rightarrow \text{Small parameter } \epsilon = \frac{E_1}{E_0} = \frac{\xi x_0^3}{\hbar\omega} = \frac{\xi\left(\frac{\hbar}{m\omega}\right)^{3/2}}{\hbar\omega}$$

(c) First order perturbation on state $|n\rangle$, $E_n^{(1)} = \hbar\omega(n+\frac{1}{2})$

$$\langle n|\hat{H}_1|n\rangle = \xi \langle n|\hat{x}^3|n\rangle = 0$$

by parity ($\hat{x}^3$ is odd)

(d) Second order

$$E_n^{(2)} = \sum_{m\neq n}' \frac{|\langle m|\hat{H}_1|n\rangle|^2}{E_n^{(0)} - E_m^{(0)}} = \frac{\xi^2}{\hbar\omega} \sum_{m\neq n}' \frac{|\langle m|\hat{x}^3|n\rangle|^2}{n-m}$$

Aside $\hat{x} = \frac{x_0}{\sqrt{2}}(\hat{a}+\hat{a}^\dagger) \Rightarrow |\langle m|\hat{x}^3|n\rangle|^2 = \left(\frac{\hbar}{2m\omega}\right)^3 |\langle m|(\hat{a}^\dagger+\hat{a})^3|n\rangle|^2$

$$\Rightarrow \boxed{E_n^{(2)} = \frac{\xi^2}{\hbar\omega}\left(\frac{\hbar}{2m\omega}\right)^3 \sum_{m\neq n}' \frac{|\langle m|(\hat{a}+\hat{a}^\dagger)^3|n\rangle|^2}{n-m}}$$

(e) $(\hat{a}+\hat{a}^\dagger)^3 = (\hat{a}+\hat{a}^\dagger)(\hat{a}^2+\hat{a}^{\dagger 2}+2\hat{N}+1)$

$= (\hat{a}^3 + \hat{a}^{\dagger 3} + \hat{a}^\dagger\hat{a}^2 + \hat{a}\hat{a}^{\dagger 2} + (\hat{a}+\hat{a}^\dagger)(2\hat{N}+1))$

After using $[\hat{a},\hat{a}^\dagger] = 1$

$$\Rightarrow (\hat{a}+\hat{a}^\dagger)^3 = \hat{a}^3 + \hat{a}^{\dagger 3} + (3\hat{N}+3)\hat{a} + 3\hat{N}\hat{a}^\dagger$$

Now
$$\langle m|\hat{a}^3|n\rangle = \sqrt{n(n-1)(n-2)}\,\delta_{m,n-3}$$
$$\langle m|\hat{a}^{\dagger 3}|n\rangle = \sqrt{(n+1)(n+2)(n+3)}\,\delta_{m,n+3}$$
$$\langle m|(3\hat{N}+3)\hat{a}|n\rangle = (3n+3)\sqrt{n}\,\delta_{m,n-1}$$
$$\langle m|3\hat{N}\hat{a}^\dagger|n\rangle = 3n\,\delta_{m,n+1}$$

Hanning around
$\hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle$
$\langle n|\hat{a}^\dagger = \sqrt{n}\,\langle n-1|$
$\hat{a}^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle$
$\langle n|\hat{a} = \sqrt{n+1}\,\langle n+1|$
$\langle n|m\rangle = \delta_{n,m}$

(Next Page)

thus $E_n^{(2)} = \frac{\xi^2 \left(\frac{\hbar}{2m\omega}\right)^3}{\hbar\omega} \left[ \frac{n(n-1)(n-2)}{3} + \frac{(n+1)(n+2)(n+3)}{-3} + \frac{9n^3}{1} + \frac{9(n+1)^3}{-1} \right]$

$$\Rightarrow \boxed{E_n^{(2)} = -\frac{\xi^2 \left(\frac{\hbar}{2m\omega}\right)^3}{\hbar\omega} \left( \frac{15}{4}\left(n+\frac{1}{2}\right) + \frac{7}{16} \right)}$$

(+) Carbon - Carbon bonds

$C_6 = 15.2 \text{ eV } \text{Å}^6$

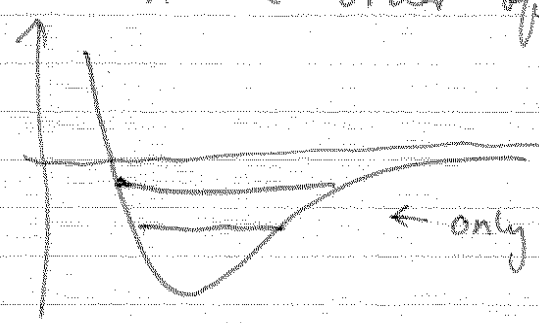
$C_{12} = 2.4 \text{ eV } \text{Å}^{12}$

Equilibrium point: $r_0 = \left(2\frac{C_{12}}{C_6}\right)^{\frac{1}{6}} = 3.8 \text{ Å}$

$\epsilon = \frac{1}{6}\frac{V_0'''}{V''} x_0 = 0.35$ for this case

$\Rightarrow$ Perturbation theory is <u>not</u> great

This is seen by the fact that $\hbar\omega$ is on the order of the binding energy



## Problem 4 Addition of spin and orbital angular momentum

An electron has both spin angular momentum, described by operator $\vec{S} = \hbar\vec{s}$ and orbital angular momentum described by operator $\vec{L} = \hbar\vec{l}$.

- We can describe the state in the "uncoupled representation" in terms of simultaneous eigenvectors of $\{\hat{l}^2, \hat{l}_z; \hat{s}^2, \hat{s}_z\}$
  $|l m_l\rangle \otimes |s, m_s\rangle$ where $s = 1/2$ for electrons $\Rightarrow m_s = +1/2, -1/2$
  Here we consider states with $l = 1 \Rightarrow m_l = 1, 0, -1$

- Alternatively, we can use the "coupled representation" in terms of simultaneous eigenvectors of $\{\hat{j}^2, \hat{j}_z, \hat{l}^2, \hat{s}^2\}$
  where $\hat{\vec{j}} = \hat{\vec{l}} + \hat{\vec{s}} \Rightarrow \hat{j}_z = \hat{l}_z + \hat{s}_z$,
  Eigenvectors: $|j m_j; ls\rangle$

Since $l=1, s=1/2$ is a common eigenvalue in both representations I will denote the short-hand for the eigenvectors

Uncoupled: $|m_l, m_s\rangle$
Coupled: $|j, m_j\rangle$
} $l, s$ understood and common to both

Let us write $\hat{j}^2$ and $\hat{j}_z$ as matricies in the uncoupled basis

We need the relationship: $\hat{j}^2 = \hat{j}\cdot\hat{j} = \hat{l}^2 + \hat{s}^2 + 2\hat{l}_z\hat{s}_z + (\hat{l}_+\hat{s}_- + \hat{l}_-\hat{s}_+$

$$\Rightarrow \hat{j}_z |m_l, m_s\rangle = (\hat{l}_z + \hat{s}_z)|m_l, m_s\rangle = (m_l + m_s)\ |m_l, m_s\rangle$$

and $$\hat{j}^2 |m_l, m_s\rangle = \{l(l+1) + s(s+1) + 2m_l m_s\}\ |m_l, m_s\rangle$$
$$+ \sqrt{l(l+1) + m_l(m_l+1)}\ \sqrt{s(s+1) - m_s(m_s-1)}\ |m_l+1, m_s-1\rangle$$
$$+ \sqrt{l(l+1) - m_l(m_l-1)}\ \sqrt{s(s+1) + m_s(m_s+1)}\ |m_l-1, m_s+1\rangle$$

**Note:** The uncoupled basis vectors $|m_\ell, m_s\rangle$ are already eigenvectors of $\hat{j}_z$, with eigenvalue $m_j = m_\ell + m_s$

Since $m_\ell = 1, 0, -1$ and $m_s = \frac{1}{2}, -\frac{1}{2}$, the possible values of $m_j$ are $m_j = \pm 3/2$ and $\pm 1/2$, with a double degeneracy for $m_j = \pm 1/2$.

$$\begin{cases} m_j = 3/2 \Rightarrow |m_\ell = 1,\ m_s = 1/2\rangle \\ m_j = 1/2 \Rightarrow |m_\ell = 0,\ m_s = 1/2\rangle \text{ or } |m_\ell = 1,\ m_s = -1/2\rangle \\ m_j = -1/2 \Rightarrow |m_\ell = 0,\ m_s = -1/2\rangle \text{ or } |m_\ell = -1,\ m_s = 1/2\rangle \\ m_j = -3/2 \Rightarrow |m_\ell = -1,\ m_s = -1/2\rangle \end{cases}$$

We can simplify the calculation by ordering the basis into orthogonal-subspaces. Since the diagonalization of $\hat{j}^2$ cannot mix states with different $m_j$, we choose the ordered basis

$$|m_\ell, m_s\rangle = \{\underbrace{|1, 1/2\rangle}_{m_j = 3/2};\ \underbrace{|0, \tfrac{1}{2}\rangle, |1, -\tfrac{1}{2}\rangle}_{m_j = \frac{1}{2}};\ \underbrace{|0, -\tfrac{1}{2}\rangle, |-1, \tfrac{1}{2}\rangle}_{m_j = -1/2};\ \underbrace{|-1, -\tfrac{1}{2}\rangle}_{m_j = -3/2}\}$$

$$\Rightarrow \hat{j}_z = \begin{bmatrix} \frac{3}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{3}{2} \end{bmatrix}, \quad \hat{j}^2 = \begin{bmatrix} \frac{15}{4} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{11}{4} & \sqrt{2} & 0 & 0 & 0 \\ 0 & \sqrt{2} & \frac{7}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{11}{4} & \sqrt{2} & 0 \\ 0 & 0 & 0 & \sqrt{2} & \frac{7}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{15}{4} \end{bmatrix}$$

Thus in each of the 2D subspaces with $m_j = 1/2$ and $m_j = -1/2$ we must diagonize the same matrix

$$M = \begin{bmatrix} \frac{11}{4} & \sqrt{2} \\ \sqrt{2} & \frac{7}{4} \end{bmatrix}$$

The secular equation for <u>both</u> $m_j = +1/2$ and $m_j = -1/2$ subspaces

$$\det(\lambda \mathbb{1} - M) = \left(\lambda - \tfrac{11}{4}\right)\left(\lambda - \tfrac{7}{4}\right) - 2 = 0$$

$$\Rightarrow \lambda^2 - \tfrac{9}{2}\lambda + \tfrac{45}{16} = 0$$

$$\Rightarrow \lambda = \tfrac{3}{4} \text{ or } \tfrac{15}{4}$$

Remember, <u>eigenvalue</u> of $\hat{j}^2$ denoted $j(j+1) \Rightarrow j = \frac{1}{2}$ or $\frac{3}{2}$

<u>Eigenvectors</u> $j = \frac{1}{2}$:

$$\begin{bmatrix} 2 & \sqrt{2} \\ \sqrt{2} & 1 \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \Rightarrow \frac{a}{b} = -\frac{1}{\sqrt{2}}$$

Normalized: $\begin{bmatrix} \frac{1}{\sqrt{3}} \\ -\sqrt{\frac{2}{3}} \end{bmatrix}$ (Remember, this is a representation given an ordered basis)

$j = \frac{3}{2}$: $\begin{bmatrix} -1 & \sqrt{2} \\ \sqrt{2} & -2 \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \Rightarrow \frac{a}{b} = \sqrt{2}$ : Normalized: $\begin{bmatrix} \sqrt{\frac{2}{3}} \\ \frac{1}{\sqrt{3}} \end{bmatrix}$

We thus have the following eigenvectors in the coupled representation:

$j = \frac{3}{2}$:

$$|j = 3/2,\ m_j = +3/2\rangle = |m_\ell = 1,\ m_s = +1/2\rangle$$

$$|j = 3/2,\ m_j = +1/2\rangle = \sqrt{\tfrac{2}{3}}\,|m_\ell = 0,\ m_s = 1/2\rangle + \sqrt{\tfrac{1}{3}}\,|m_\ell = 1,\ m_s = -1/2\rangle$$

$$|j = 3/2,\ m_j = -1/2\rangle = \sqrt{\tfrac{2}{3}}\,|m_\ell = 0,\ m_s = -1/2\rangle + \sqrt{\tfrac{1}{3}}\,|m_\ell = -1,\ m_s = +1/2\rangle$$

$$|j = 3/2,\ m_j = -3/2\rangle = |m_\ell = -1,\ m_s = -1/2\rangle$$

$j = \frac{1}{2}$:

$$|j = 1/2,\ m_j = +1/2\rangle = \sqrt{\tfrac{1}{3}}\,|m_\ell = 0,\ m_s = 1/2\rangle - \sqrt{\tfrac{2}{3}}\,|m_\ell = 1,\ m_s = -1/2\rangle$$

$$|j = 1/2,\ m_j = -1/2\rangle = \sqrt{\tfrac{1}{3}}\,|m_\ell = 0,\ m_s = -1/2\rangle - \sqrt{\tfrac{2}{3}}\,|m_\ell = -1\ m_s = +1/2\rangle$$

These agree with C-T, Complement $A_X$ (vol II) eqns. 36-a)

Note:

- The possible eigenvalues of $j$ range from $j_{max} = l+s = \frac{3}{2}$ to $j_{min} = |l-s| = \frac{1}{2}$ as expected
- The Clebsch-Gordan coefficients are now given

$$\langle j\, m_j \,|\, l\, m_l;\, s\, m_s\rangle = \langle l\, m_l;\, s\, m_s \,|\, j\, m_j\rangle$$

$$\Rightarrow \langle \tfrac{3}{2}\ \tfrac{3}{2} \,|\, 1\,1;\, \tfrac{1}{2}\ \tfrac{1}{2}\rangle = \langle \tfrac{3}{2}, -\tfrac{3}{2} \,|\, 1\,{-1},\, \tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle = 1$$

$$\left|\langle \tfrac{3}{2}\ \tfrac{1}{2} \,|\, 1\,1,\, \tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle\right| = \left|\langle \tfrac{3}{2}, -\tfrac{1}{2} \,|\, 1\,{-1},\, \tfrac{1}{2}\ \tfrac{1}{2}\rangle\right| = \left|\langle \tfrac{1}{2}\ \tfrac{1}{2} \,|\, 1\,0;\, \tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle\right| = \left|\langle \tfrac{1}{2}\ {-\tfrac{1}{2}} \,|\, 1\,0,\, \tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle\right| = \sqrt{\tfrac{1}{3}}$$

$$\left|\langle \tfrac{3}{2}\ \tfrac{1}{2} \,|\, 1\,0;\, \tfrac{1}{2}\ \tfrac{1}{2}\rangle\right| = \left|\langle \tfrac{3}{2}, -\tfrac{1}{2} \,|\, 1\,0,\, \tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle\right| = \left|\langle \tfrac{1}{2}\ \tfrac{1}{2} \,|\, 1\,1,\, \tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle\right| = \left|\langle \tfrac{1}{2}\ \tfrac{1}{2} \,|\, 1\,{-1},\, \tfrac{1}{2}\ \tfrac{1}{2}\rangle\right| = \sqrt{\tfrac{2}{3}}$$

We cannot assure the sign of CG coefficient is consistent with our phase convention by this method.

(b) We can easily find the matrix elements of $\hat{\vec{l}}\cdot\hat{\vec{s}}$ by noting

$$\hat{\vec{j}}^2 = (\hat{\vec{l}}+\hat{\vec{s}})\cdot(\hat{\vec{l}}+\hat{\vec{s}}) = \hat{l}^2 + \hat{s}^2 + 2\hat{\vec{l}}\cdot\hat{\vec{s}}$$

$$\Rightarrow \hat{\vec{l}}\cdot\hat{\vec{s}} = \frac{1}{2}\left(\hat{\vec{j}}^2 - \hat{\vec{l}}^2 - \hat{\vec{s}}^2\right)$$

$$\Rightarrow \langle j' m_j';\, l, s \,|\, \hat{\vec{l}}\cdot\hat{\vec{s}} \,|\, j\, m_j;\, l\, s\rangle = \frac{1}{2}\left(j(j+1) - l(l+1) - s(s+1)\right)\delta_{jj'}\delta_{m_j m_j'}$$

$$\Rightarrow \langle j=\tfrac{1}{2}\ m_j;\, l, s \,|\, \hat{\vec{l}}\cdot\hat{\vec{s}} \,|\, j={-\tfrac{1}{2}}, m_j, l, s\rangle = -2$$

$$\langle j=\tfrac{3}{2}, m_j;\, l\, s \,|\, \hat{\vec{l}}\cdot\hat{\vec{s}} \,|\, j=\tfrac{3}{2}, m_j, l\, s\rangle = 1$$

$$= 0 \quad \text{Herwise}$$