Physics 449 Exam 1 Spring 2018 Due 4/6/2018 W10F

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W10T

In[32]:=
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<< "http://www.physics.wisc.edu/~tgwalker/448defs.m"
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1) Sr has 2 valence electrons. Some of its important low-lying excited states are denoted $5s5p\,^3P_j$. -

a) Possible values of j

Given ^3P_j, $S = s = 1$, $L = l = 1 \to J_{\max} = L + S = 2$; $J_{\min} = |L - S| = 0 \to j = 0, 1, 2$.

b) The total wavefunction -

$j_{\max} = m = 2$
$\psi = \psi_{5s}\,\psi_{5p} = \frac{P_{5s}}{r_1} Y_{s,0} \frac{P_{5p}}{r_2} Y_{p,1}$

From the handout “Atomic State Notation”:

$$\left|\,^{2S+1}L_J\right\rangle = \sum_{m_L m_S} C^{J\,m}_{L m_L\, S m_S} \left|L\, m_L\, S\, m_S\right\rangle;$$

$$\left\langle \mathbf{r} \middle| n L\,^{2S+1}L_J\right\rangle = \sum_{m_L m_s} C^{J\,m}_{L m_L\, s\, m_s} \left\langle \mathbf{r} \middle| n L\, m_L\, 1/2\, m_s\right\rangle = \sum_{m_L m_s} C^{J\,m}_{L m_L\, s\, m_s} \frac{P_{nL}(r)}{r} Y_{Lm}(\theta, \phi)\, \left|m_s\right\rangle$$

The total wavefunction is given by:

$$\psi(5s_{j_1}) = \frac{P_{5s}(r)}{r} \sum_{m_l m_s} C^{J_1\, m_{j_1}}_{0\, m_l\, \frac{1}{2} m_s}\, Y_{0\, m_l}(\theta, \phi) \left|m_s\right\rangle$$

$$\psi(5p_{j_2}) = \frac{P_{5p}(r)}{r} \sum_{m_l m_s} C^{J_2\, m_{j_2}}_{1\, m_l\, \frac{1}{2} m_s}\, Y_{1\, m_l}(\theta, \phi) \left|m_s\right\rangle$$

for $m = 2$, letting $\chi_{m_s} = \left|m_s\right\rangle$

```
Sum[P5s/r Y0,ml χms ClebschGordan[{0, ml}, {1/2, ms}, {1/2, 1/2}],
   {ms, -1/2, 1/2}, {ml, 0, 0}] // Simplify
```

... ClebschGordan: ThreeJSymbol[{0, 0}, {1/2, -1/2}, {1/2, -1/2}] is not physical.

$$\frac{P_{5\,s}\,\chi_{\frac{1}{2}}\,Y_{0,0}}{r}$$

```
Sum[P5p/r Y1,ml χms ClebschGordan[{1, ml}, {1/2, ms}, {3/2, 3/2}],
   {ms, -1/2, 1/2}, {ml, -1, 1}] // Simplify
```

... ClebschGordan: ThreeJSymbol[{1, -1}, {1/2, -1/2}, {3/2, -3/2}] is not physical.

... ClebschGordan: ThreeJSymbol[{1, 0}, {1/2, -1/2}, {3/2, -3/2}] is not physical.

... ClebschGordan: ThreeJSymbol[{1, 1}, {1/2, -1/2}, {3/2, -3/2}] is not physical.

... General: Further output of ClebschGordan::phy will be suppressed during this calculation.

$$\frac{P_{5\,p}\,\chi_{\frac{1}{2}}\,Y_{1,1}}{r}$$

$$\psi = \frac{P_{5s}\,Y_{0,0}(\theta_1,\phi_1)}{r_1}\,\frac{P_{5p}\,Y_{1,1}(\theta_2,\phi_2)}{r_2}\,\chi_{1/2}$$

Plug these terms in,

In[33]:=
```
ψ = P5,0[r1, 2] P5,1[r2, 2] SphericalHarmonicY[0, 0, θ1, ϕ1]
   SphericalHarmonicY[1, 1, θ2, ϕ2] χ1/2 // FullSimplify
```

Out[33]=
$$-\frac{1}{10\,986\,328\,125\,\pi}32\,e^{-\frac{2}{5}(r1+r2)+i\,\phi 2}\,r1\,(9375+8\,r1\,(-1875+2\,r1\,(375+2\,(-25+r1)\,r1)))\,r2^2\,(-1875+r2\,(1125+4\,r2\,(-45+2\,r2)))\,\mathrm{Sin}[\theta 2]\,\chi_{\frac{1}{2}}$$

c) Simplify: -

$$\left\langle 5s5p\,^3P_j \right| \frac{1}{r_{12}} \left| 5s5p\,^3P_j \right\rangle =$$

$$\int_{r_2}\int_{r_1}\int_{\Omega_2}\int_{\Omega_1} \frac{P_{5s}}{r_1} Y_{0,0}{}^{*} \frac{P_{5p}}{r_2} Y_{1,1}{}^{*} \frac{1}{\sqrt{r_1{}^2+r_2{}^2+2\,r_1\,r_2\,\mathrm{Cos}[\theta_{12}]}} \frac{P_{5s}}{r_1} Y_{0,0} \frac{P_{5p}}{r_2} Y_{1,1}\, r_1{}^2\, r_2{}^2\, \mathrm{Sin}[\theta]\, d\Omega_1\, d\Omega_2\, dr_1\, dr_2$$

$$= \int_{r_2}\int_{r_1}\int_{\Omega_2}\int_{\Omega_1} \frac{P_{5s}}{r_1} Y_{0,0}{}^{*} \frac{P_{5p}}{r_2} Y_{1,1}{}^{*}$$

$$\sum_{l,m} \frac{4\pi}{2l+1} \frac{r_<{}^l}{r_>{}^{l+1}} (-1)^m\, Y_{l,m}(l_1)\, Y_{l,\overline{m}}(l_2) \frac{P_{5s}}{r_1} Y_{0,0} \frac{P_{5p}}{r_2} Y_{1,1}\, r_1{}^2\, r_2{}^2\, \mathrm{Sin}[\theta]\, d\Omega_1\, d\Omega_2\, dr_1\, dr_2$$

$$= \int_{r_2}\int_{r_1} P_{5s}\, P_{5p} \frac{1}{r_{12}} P_{5s}\, P_{5p}\, dr_1\, dr_2\, Y_{5,0}{}^{*}\, Y_{5,1}{}^{*}\, Y_{5,0}\, Y_{5,1}\, \mathrm{Sin}[\theta]\, d\Omega_1\, d\Omega_2$$

$$\simeq \frac{P_{5s}{}^2(r_1)\, P_{5p}{}^2(r_2)}{r_>}$$

Numerically,

```
In[34]:= Integrate[P5,0[r1, 2]^2 Min[1/r1, 1/r2] P5,1[r2, 2]^2, {r1, 0, ∞}, {r2, 0, ∞}] // N

Out[34]= 0.0482935
```

2)

a)

$\hat{H} = \frac{\hat{p}}{2M} + V(r)$. Solve for the Schrodinger equation $\left(\frac{\hat{p}}{2M} + V(r)\right)\psi = E\,\psi$, where $p = \frac{-\hbar^2}{2M}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) + \frac{l(l+1)}{2Mr^2}\hbar^2$, $\psi = \frac{P(r)}{r} Y_{l\,m}$

From the handout "3-D Potentials," for particle in the spherically symmetric potential , $V = 0$ for $r < a$. Setting $E = \hbar^2\,\epsilon/\mu$, the solutions to the Schrodinger equation are

```
DSolve[{-1/2 P''[r] + (l (l + 1))/(2 r^2) P[r] == ϵ P[r]}, P[r], r]

{{P[r] →
   √r BesselJ[1/2 (1 + 2 l), √2 r √ϵ] C[1] + √r BesselY[1/2 (1 + 2 l), √2 r √ϵ] C[2]}}
```

The second kind of Bessel function should vanish to fulfill the boundary condition. The solution is given by

$$P(r) = C_1 \sqrt{r}\; J_q(k\,a)$$

To find zeros, let $J_q(k\,a) = 0 \to k = \frac{1}{a} x_{q,n}$, where $x_{q,n}$ to be the n^{th} zero of the q^{th} Bessel function; let

$x_{q,n} = n\,\pi$. When $l = 0$, it follows that

$$E_{n,l=0} = \frac{\hbar^2 k^2}{2M} = \frac{\hbar^2}{2M}\left(\frac{n\,\pi}{a}\right)^2 \text{ (Townsend 10.72)}$$

Compare with $E_{n,l} = \frac{\hbar^2 \pi^2}{2M}(n + s_l)^2 \to s_0 = 0$

b) _

Given the same value of n, the larger l corresponds to the larger energy. Given that $l = 0, 1, 2$, it follows that

$$E_{n,0} < E_{n,1} < E_{n,2}$$

Given that $E_{n,l} = \frac{\hbar^2 \pi^2}{2M}(n + s_l)^2$, then

$$s_0 < s_1 < s_2$$

c) -

In an external magnetic field,

$$\hat{H}_B = -\hat{\mu}\cdot B = \frac{|e|B}{2m_e c}\left(\hat{J}_z + \hat{S}_z\right) \qquad \text{(Townsend 11.106)}$$

$$E_B^{(1)} = \frac{|e|B}{2m_e c}\left\langle j = l \pm \tfrac{1}{2},\, m_j\right|\left(\hat{J}_z + \hat{S}_z\right)\left|j = l \pm \tfrac{1}{2},\, m_j\right\rangle \qquad \text{(T 11.107)}$$

$$\langle S_z\rangle = \pm\frac{m_j\,\hbar}{2l+1} \qquad \text{(T 11.108)}$$

$$\langle J_z\rangle = m_j\,\hbar \qquad \text{(T 3.25b)}$$

Given that $s = 0$, with $|s - l| \le j \le s + l \to j = l$, then

$$\langle S_z\rangle = \pm\frac{m_j\,\hbar}{2j+1} = 0$$

The first order correction is given by

$$\left\langle j,\, m_j\right|\hat{H}_B\left|j,\, m_j\right\rangle = m_j\,\hbar\,\frac{|e|B}{2m_e c} = m_l\,\hbar\,\frac{|e|B}{2m_e c}$$

d)

Given three spin-0 particles, two of them can occupy the same state. The energy of three particles in the first excited states separately is given by

$$E_{10} = \frac{\pi^2\hbar^2}{2Ma^2}(1 + \delta_0)^2;\, E_{10} = \frac{\pi^2\hbar^2}{2Ma^2}(1 + \delta_0)^2;\, E_{11} = \frac{\pi^2\hbar^2}{2Ma^2}(1 + \delta_1)^2$$

The total energy in the first excited state is given by

$$E_1 = \frac{\pi^2\hbar^2}{2Ma^2}\left[2(1 + \delta_0)^2 + (1 + \delta_1)^2\right]$$

The states of the particles can be arranged as

$$\left|1s;1s;1p\right\rangle,\ \left|1s;1p;1s\right\rangle,\ \left|1p;1s;1s;\right\rangle$$

Hence, the degeneracy = 3.

3)

a)

When an electric field $V = e\,x\,\varepsilon$ is applied to a Rb atom, $\left|5\,s\right\rangle + \sum_m \epsilon_{l\,m} \left|5\,l\,m\right\rangle$ only $5\,p$ state contributes to the energy shift. Hence, $l = 1$, $m_l = -1, 0, 1$.

By the calculation in the part *b*), only terms

$$\left\langle 5\,s\,0\right| x \left|5\,p\,-1\right\rangle, \left\langle 5\,s\,0\right| x \left|5\,p\,1\right\rangle, \left\langle 5\,p\,-1\right| x \left|5\,s\,0\right\rangle, \left\langle 5\,p\,1\right| x \left|5\,s\,0\right\rangle$$

provide perturbations. When $m = 0$, the term does not provide the perturbation.

Also, calculate

$$\left\langle 5\,s\,0\right| x \left|5\,d\,1\right\rangle = \left\langle 5\,s\,0\right| x \left|5\,d\,2\right\rangle =. .. = 0$$

It suggests that when $l > 0$, the terms do not contribute to the perturbation.

Hence, $l = 1$, $m_l = -1, 1$.

b)

Let $H^{(0)}$ be the unperturbed Hamiltonian.
By perturbation theory, the first-order correction to the energy eigenstates is given by

$$\left|\psi_n\right\rangle = \left|\varphi_n{}^{(0)}\right\rangle + \lambda \sum_{k \neq n} \left|\varphi_k{}^{(0)}\right\rangle \frac{\left\langle \varphi_k{}^{(0)}\right| \hat{H}_1 \left|\varphi_n{}^{(0)}\right\rangle}{E_n{}^{(0)} - E_k{}^{(0)}} + O(\lambda^2) \text{ (Townsend 11.23)}$$

It follows that

$$\epsilon_{l\,m} = \frac{\left\langle \varphi_k{}^{(0)}\right| \hat{H}_1 \left|\varphi_n{}^{(0)}\right\rangle}{E_n{}^{(0)} - E_k{}^{(0)}} = e\,\varepsilon \frac{\left\langle 5\,p\,m\right| x \left|5\,s\,0\right\rangle}{E_{5\,s\,0} - E_{5\,p\,m}}, \text{ where } m = -1, 1.$$

The unperturbed energy levels are

$$\left\langle 5\,s\,0\right| H^{(0)} \left|5\,s\,0\right\rangle, \left\langle 5\,p\,0\right| H^{(0)} \left|5\,p\,0\right\rangle, \left\langle 5\,p\,1\right| H^{(0)} \left|5\,p\,1\right\rangle$$

c)

It follows from *b*),

$$\left|\psi_n\right\rangle = \left|\varphi_n{}^{(0)}\right\rangle + \lambda \sum_{k \neq n} \left|\varphi_k{}^{(0)}\right\rangle \frac{\left\langle \varphi_k{}^{(0)}\right| \hat{H}_1 \left|\varphi_n{}^{(0)}\right\rangle}{E_n{}^{(0)} - E_k{}^{(0)}} + O(\lambda^2)$$

$$= \left|5\,s\,0\right\rangle + \left|5\,p\,-1\right\rangle e\,\varepsilon \frac{\left\langle 5\,p\,-1\right| x \left|5\,s\,0\right\rangle}{E_{5\,s\,0} - E_{5\,p\,-1}} + \left|5\,p\,0\right\rangle e\,\varepsilon \frac{\left\langle 5\,p\,0\right| x \left|5\,s\,0\right\rangle}{E_{5\,s\,0} - E_{5\,p\,0}} + \left|5\,p\,1\right\rangle e\,\varepsilon \frac{\left\langle 5\,p\,1\right| x \left|5\,s\,0\right\rangle}{E_{5\,s\,0} - E_{5\,p\,1}}$$

$$-e\langle x\rangle = -\frac{\langle V\rangle}{\varepsilon} = -e\left\langle \psi_n \middle| x \middle| \psi_n \right\rangle$$

$$= -e\left(\left\langle 5\,s\,0\right| + \left\langle 5\,p-1\right|\, e\,\varepsilon\,\frac{\left\langle 5\,p-1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p-1}} + \left\langle 5\,p\,0\right|\, e\,\varepsilon\,\frac{\left\langle 5\,p\,0\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p0}} + \left\langle 5\,p\,1\right|\, e\,\varepsilon\,\frac{\left\langle 5\,p\,1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p1}}\right)$$

$$x\left(\left|5\,s\,0\right\rangle + \left|5\,p-1\right\rangle e\,\varepsilon\,\frac{\left\langle 5\,p-1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p-1}} + \left|5\,p\,0\right\rangle e\,\varepsilon\,\frac{\left\langle 5\,p\,0\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p0}} + \left|5\,p\,1\right\rangle e\,\varepsilon\,\frac{\left\langle 5\,p\,1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p1}}\right)$$

$$= -e\Bigg[\left\langle 5\,s\,0\middle| x \middle| 5\,s\,0\right\rangle$$

$$+ e\,\varepsilon\Bigg(\frac{\left\langle 5\,p-1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p-1}}\left\langle 5\,s\,0\middle| x \middle| 5\,p-1\right\rangle + \frac{\left\langle 5\,p\,0\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p0}}\left\langle 5\,s\,0\middle| x \middle| 5\,p\,0\right\rangle +$$

$$\frac{\left\langle 5\,p\,1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p1}}\left\langle 5\,s\,0\middle| x \middle| 5\,p\,1\right\rangle + \frac{\left\langle 5\,p-1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p-1}}\left\langle 5\,p-1\middle| x \middle| 5\,s\,0\right\rangle +$$

$$\frac{\left\langle 5\,p\,0\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p0}}\left\langle 5\,p\,0\middle| x \middle| 5\,s\,0\right\rangle + \frac{\left\langle 5\,p\,1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p1}}\left\langle 5\,p\,1\middle| x \middle| 5\,s\,0\right\rangle\Bigg)$$

$$+ (e\,\varepsilon)^2\Bigg(\frac{\left\langle 5\,p-1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p-1}}\Bigg(\frac{\left\langle 5\,p-1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p-1}}\left\langle 5\,p-1\middle| x \middle| 5\,p-1\right\rangle +$$

$$\frac{\left\langle 5\,p\,0\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p0}}\left\langle 5\,p-1\middle| x \middle| 5\,p\,0\right\rangle + \frac{\left\langle 5\,p\,1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p1}}\left\langle 5\,p-1\middle| x \middle| 5\,p\,1\right\rangle\Bigg)$$

$$+ \frac{\left\langle 5\,p\,0\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p0}}\Bigg(\frac{\left\langle 5\,p-1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p-1}}\left\langle 5\,p\,0\middle| x \middle| 5\,p-1\right\rangle + \frac{\left\langle 5\,p\,0\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p0}}\left\langle 5\,p\,0\middle| x \middle| 5\,p\,0\right\rangle +$$

$$\frac{\left\langle 5\,p\,1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p1}}\left\langle 5\,p\,0\middle| x \middle| 5\,p\,1\right\rangle\Bigg)$$

$$+ \frac{\left\langle 5\,p\,1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p1}}\Bigg(\frac{\left\langle 5\,p-1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p-1}}\left\langle 5\,p\,1\middle| x \middle| 5\,p-1\right\rangle + \frac{\left\langle 5\,p\,0\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p0}}\left\langle 5\,p\,1\middle| x \middle| 5\,p\,0\right\rangle +$$

$$\frac{\left\langle 5\,p\,1\middle| x \middle| 5\,s\,0\right\rangle}{E_{5s0}-E_{5p1}}\left\langle 5\,p\,1\middle| x \middle| 5\,p\,1\right\rangle\Bigg)\Bigg)\Bigg]$$

To get different $\left\langle 5\,l\,m\middle| x \middle| 5\,l'\,m'\right\rangle$:

$$x = r\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]$$

$$\left\langle 5\,l\,m\middle| x \middle| 5\,l'\,m'\right\rangle = \int_r\int_\Omega \frac{P_{5l}}{r}\,Y_{lm}{}^{*}(\theta,\phi)\,r\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\phi]\,\frac{P_{5l'}}{r}\,Y_{l'm'}(\theta,\phi)\,r^2\,d\Omega\,dr$$

```
P_{n_, l_}[r_, Z_] := Sqrt[Z] * P_{n, l}[Z * r];
```

```
Integrate[P_{5,0}[r, 1] SphericalHarmonicY[0, 0, θ, ϕ]* r Cos[ϕ] Sin[θ] P_{5,0}[r, 1]
  SphericalHarmonicY[0, 0, θ, ϕ] Sin[θ], {r, 0, ∞}, {θ, 0, π}, {ϕ, 0, 2 π}]
```

```
0
```

```
Integrate[P5,0[r, 1] SphericalHarmonicY[0, 0, θ, ϕ]* r Cos[ϕ] Sin[θ] P5,1[r, 1]
  SphericalHarmonicY[1, -1, θ, ϕ] Sin[θ], {r, 0, ∞}, {θ, 0, π}, {ϕ, 0, 2 π}]

Integrate[P5,0[r, 1] SphericalHarmonicY[0, 0, θ, ϕ]* r Cos[ϕ] Sin[θ] P5,1[r, 1]
  SphericalHarmonicY[1, 0, θ, ϕ] Sin[θ], {r, 0, ∞}, {θ, 0, π}, {ϕ, 0, 2 π}]

Integrate[P5,0[r, 1] SphericalHarmonicY[0, 0, θ, ϕ]* r Cos[ϕ] Sin[θ] P5,1[r, 1]
  SphericalHarmonicY[1, 1, θ, ϕ] Sin[θ], {r, 0, ∞}, {θ, 0, π}, {ϕ, 0, 2 π}]
```

```
15
```

```
0
```

```
-15
```

$\left\langle 5\,s\,0 \middle| \, x \, \middle| 5\,p\,-1 \right\rangle = 15$

$\left\langle 5\,s\,0 \middle| \, x \, \middle| 5\,p\,1 \right\rangle = -15$

```
Integrate[P5,1[r, 1] SphericalHarmonicY[1, -1, θ, ϕ]* r Cos[ϕ] Sin[θ] P5,0[r, 1]
  SphericalHarmonicY[0, 0, θ, ϕ] Sin[θ], {r, 0, ∞}, {θ, 0, π}, {ϕ, 0, 2 π}]

Integrate[P5,1[r, 1] SphericalHarmonicY[1, 0, θ, ϕ]* r Cos[ϕ] Sin[θ] P5,0[r, 1]
  SphericalHarmonicY[0, 0, θ, ϕ] Sin[θ], {r, 0, ∞}, {θ, 0, π}, {ϕ, 0, 2 π}]

Integrate[P5,1[r, 1] SphericalHarmonicY[1, 1, θ, ϕ]* r Cos[ϕ] Sin[θ] P5,0[r, 1]
  SphericalHarmonicY[0, 0, θ, ϕ] Sin[θ], {r, 0, ∞}, {θ, 0, π}, {ϕ, 0, 2 π}]
```

```
15
```

```
0
```

```
-15
```

$\left\langle 5\,p\,1 \middle| \, x \, \middle| 5\,s\,0 \right\rangle = 15$

$\left\langle 5\,p\,1 \middle| \, x \, \middle| 5\,s\,0 \right\rangle = -15$

```
Integrate[P5,1[r, 1] SphericalHarmonicY[1, -1, θ, ϕ]* r Cos[ϕ] Sin[θ] P5,1[r, 1]
  SphericalHarmonicY[1, 1, θ, ϕ] Sin[θ], {r, 0, ∞}, {θ, 0, π}, {ϕ, 0, 2 π}]
Integrate[P5,1[r, 1] SphericalHarmonicY[1, -1, θ, ϕ]* r Cos[ϕ] Sin[θ] P5,1[r, 1]
  SphericalHarmonicY[1, 0, θ, ϕ] Sin[θ], {r, 0, ∞}, {θ, 0, π}, {ϕ, 0, 2 π}]
Integrate[P5,1[r, 1] SphericalHarmonicY[1, -1, θ, ϕ]* r Cos[ϕ] Sin[θ] P5,1[r, 1]
  SphericalHarmonicY[1, -1, θ, ϕ] Sin[θ], {r, 0, ∞}, {θ, 0, π}, {ϕ, 0, 2 π}]
```

```
0
```

```
0
```

```
0
```

Plug these values in,

$$-e\langle x\rangle$$
$$= -e\left[e\,\varepsilon\left(\frac{15}{E_{5s0}-E_{5p-1}}15+\frac{15}{E_{5s0}-E_{5p1}}15+\frac{15}{E_{5s0}-E_{5p-1}}15+\frac{15}{E_{5s0}-E_{5p1}}15\right)\right.$$
$$= -\frac{4*225\,e^2\,\varepsilon}{-0.0573139\text{ Hartree}}\left(\frac{15}{E_{5s0}-E_{5p-1}}15+\frac{15}{E_{5s0}-E_{5p1}}15+\frac{15}{E_{5s0}-E_{5p-1}}15+\frac{15}{E_{5s0}-E_{5p1}}15\right)$$

From NIST,

$$E_{5s0}-E_{5p0} = -0.0573139\text{ Hartree}$$

```
-1/2 * 0.114627827
```

```
-0.0573139
```

```
4 * 225
```

```
900
```

It follows that

$$-e\langle x\rangle = \frac{900\,e^2\,\varepsilon}{0.0573139\text{ Hartree}}$$

4) $\left\langle \| 2\,sd;\,1\,su;\,2\,su\| \,\middle|\, \hat{S}^2 \,\middle|\, \| 2\,s\,d;\,1\,s\,u;\,2\,s\,u\| \right\rangle$

$$\left|\,\|2\,s\,d;1\,s\,u;2\,s\,u\|\right\rangle$$
$$= \frac{1}{\sqrt{6}}\Big(\left|2\,s\,d;1\,s\,u;2\,s\,u\right\rangle+\left|2\,s\,u;2\,s\,d;1\,s\,u\right\rangle+\left|1\,s\,u;2\,s\,d;2\,s\,u\right\rangle$$
$$-\left|1\,s\,u;2\,s\,u;2\,s\,d\right\rangle-\left|2\,s\,d;2\,s\,u;1\,s\,u\right\rangle-\left|2\,s\,u;1\,s\,u;2\,s\,d\right\rangle\Big)$$

$$\hat{S}^2 = (S_1+S_2+S_3)^2 = S_1^2+S_1\,S_2+S_1\,S_3+S_2\,S_1+S_2^2+S_2\,S_3+S_3\,S_1+S_3\,S_2+S_3^2$$

$S_i^2\left|s_i\,m_{s_i}\right\rangle = \hbar^2\,s_i(s_i+1)\left|s_i\,m_{s_i}\right\rangle$; $S_i\left|s_i\,m_{s_i}\right\rangle = \hbar\sqrt{s_i(s_i+1)}\left|s_i\,m_{s_i}\right\rangle$, where $i = 1, 2, 3$, $s_1 = s_2 = s_3 = \frac{1}{2}$

$$\hat{S}^2 \left| \, || 2\,s\,d; 1\,s\,u; 2\,s\,u || \right\rangle$$
$$= \frac{1}{\sqrt{6}} \left(S_1{}^2 + S_1\,S_2 + S_1\,S_3 + S_2\,S_1 + S_2{}^2 + S_2\,S_3 + S_3\,S_1 + S_3\,S_2 + S_3{}^2\right)$$
$$\left(\left| 2\,s\,d; 1\,s\,u; 2\,s\,u \right\rangle + \left| 2\,s\,u; 2\,s\,d; 1\,s\,u \right\rangle + \left| 1\,s\,u; 2\,s\,d; 2\,s\,u \right\rangle - \right.$$
$$\left. \left| 1\,s\,u; 2\,s\,u; 2\,s\,d \right\rangle - \left| 2\,s\,d; 2\,s\,u; 1\,s\,u \right\rangle - \left| 2\,s\,u; 1\,s\,u; 2\,s\,d \right\rangle \right)$$

$$S_1{}^2 \left| 2\,s\,d; 1\,s\,u; 2\,s\,u \right\rangle = \hbar^2\,s_1(s_1+1) \left| 2\,s\,d; 1\,s\,u; 2\,s\,u \right\rangle = \hbar^2\,\frac{1}{2}\,\frac{3}{2} = \frac{3}{4}\,\hbar^2 \left| 2\,s\,d; 1\,s\,u; 2\,s\,u \right\rangle$$
$$S_1\,S_2 \left| 2\,s\,d; 1\,s\,u; 2\,s\,u \right\rangle = \frac{3}{4}\,\hbar^2$$

Similarly for other product terms. It follows that

$$\hat{S}^2 \left| \, || 2\,s\,d; 1\,s\,u; 2\,s\,u || \right\rangle$$
$$= \frac{1}{6} \left(3 * \frac{3}{4} + 6 * \frac{3}{4}\right) \hbar^2 \left| \, || 2\,s\,d; 1\,s\,u; 2\,s\,u || \right\rangle$$
$$= \frac{9}{8}\,\hbar^2 \left| \, || 2\,s\,d; 1\,s\,u; 2\,s\,u || \right\rangle$$

Then

$$\left\langle || 2\,\mathrm{sd}; 1\,\mathrm{su}; 2\,\mathrm{su} || \right| \hat{S}^2 \left| \, || 2\,s\,d; 1\,s\,u; 2\,s\,u || \right\rangle = \frac{9}{8}\,\hbar^2$$

Check by applying the method in the Li project:

In[36]:=

```
P_{n_,l_,zz_}[r_] := √zz P_{n,l}[zz r]
H12a[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  δ_{n3,n6} δ_{n2,n5} Integrate[P_{n1,0,zz}[r] (-1/2 ∂_{r,r} P_{n4,0,zz}[r] - Z/r P_{n4,0,zz}[r]), {r, 0, ∞}];
H12b[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  δ_{n3,n6} δ_{n1,n4} Integrate[P_{n2,0,zz}[r] (-1/2 ∂_{r,r} P_{n5,0,zz}[r] - Z/r P_{n5,0,zz}[r]), {r, 0, ∞}];
H12c[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  δ_{n1,n4} δ_{n2,n5} Integrate[P_{n3,0,zz}[r] (-1/2 ∂_{r,r} P_{n6,0,zz}[r] - Z/r P_{n6,0,zz}[r]), {r, 0, ∞}];
Vb12[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_] := δ_{n3,n6} Integrate[
    P_{n1,0,zz}[r1] P_{n2,0,zz}[r2] Min[1/r2, 1/r1] P_{n4,0,zz}[r1] P_{n5,0,zz}[r2], {r2, 0, ∞}, {r1, 0, ∞}];
Vb13[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_] := δ_{n2,n5} Integrate[
    P_{n1,0,zz}[r1] P_{n3,0,zz}[r3] Min[1/r3, 1/r1] P_{n4,0,zz}[r1] P_{n6,0,zz}[r3], {r3, 0, ∞}, {r1, 0, ∞}];
Vb23[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_] := δ_{n1,n4} Integrate[
    P_{n2,0,zz}[r2] P_{n3,0,zz}[r3] Min[1/r2, 1/r3] P_{n5,0,zz}[r2] P_{n6,0,zz}[r3], {r2, 0, ∞}, {r3, 0, ∞}];
H12d[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  H12d[{n1, n2, n3}, {n4, n5, n6}, zz, Z] =
   (H12a[{n1, n2, n3}, {n4, n5, n6}, zz, Z] + H12b[{n1, n2, n3}, {n4, n5, n6}, zz, Z] +
      H12c[{n1, n2, n3}, {n4, n5, n6}, zz, Z] + Vb12[{n1, n2, n3}, {n4, n5, n6}, zz] +
      Vb13[{n1, n2, n3}, {n4, n5, n6}, zz] + Vb23[{n1, n2, n3}, {n4, n5, n6}, zz]) -
    (H12a[{n1, n2, n3}, {n4, n6, n5}, zz, Z] + H12b[{n1, n2, n3}, {n4, n6, n5}, zz, Z] +
      H12c[{n1, n2, n3}, {n4, n6, n5}, zz, Z] + Vb12[{n1, n2, n3}, {n4, n6, n5}, zz] +
      Vb13[{n1, n2, n3}, {n4, n6, n5}, zz] + Vb23[{n1, n2, n3}, {n4, n6, n5}, zz]);
```

The value of $\hat{S}^2$ by applying the method in Li project:

In[44]:=

```
H12d[{2, 1, 2}, {2, 1, 2}, 2.688776938, 3] * 9/8 * H12d[{2, 1, 2}, {2, 1, 2}, 2.688776938, 3]
```

Out[44]=

```
30.4595
```

The value from this problem by calculating through the Slater Determinant:

In[46]:=

```
(-5.20336)^2 (9/8)
```

Out[46]=

```
30.4593
```

They match with each other.