Part 2. Multiple Choice/Short Answer

Except when noted otherwise, you should use the Born-Oppenheimer approximation and atomic units throughout Parts 2 and 3 of this exam.

1-2. Write expressions for each of the following operators in SI units.

Quantity	Quantum-Mechanical Operator in SI units
nuclear kinetic energy, $\hat{T}_n$	$\sum_{\alpha=1}^{P} -\frac{\hbar^2}{2m_\alpha}\nabla_\alpha^2$
electronic kinetic energy, $\hat{T}_e$	$\sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\nabla_i^2$
nuclear-electron attraction energy, $\hat{V}_{ne}$	$\sum_{\alpha=1}^{P}\sum_{i=1}^{N}\frac{-Z_\alpha e^2}{4\pi\varepsilon_0 \lvert \boldsymbol{r}_i - \boldsymbol{R}_\alpha \rvert}$
nuclear-nuclear repulsion energy, $\hat{V}_{nn}$	$\sum_{\alpha=1}^{P-1}\sum_{\beta=\alpha+1}^{P}\frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0 \lvert \boldsymbol{R}_\alpha - \boldsymbol{R}_\beta \rvert}$
electron-electron repulsion energy, $\hat{V}_{ee}$	$\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{e^2}{4\pi\varepsilon_0 \lvert \boldsymbol{r}_i - \boldsymbol{r}_j \rvert}$

We wrote the "electronic" Schrödinger equation for the P-atom, N-electron molecule in the Born-Oppenheimer approximation as

$$\left(\hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn}\right)\psi_e\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N; \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_P\right)$$
$$= U_{BO}\left(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_P\right)\psi_e\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N; \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_P\right)$$

3. **Using the above notation and the notation from problems 1 and 2, write the Schrödinger equation for the nuclei in the Born-Oppenheimer Approximation.**

$$\left(\hat{T}_n + U_{BO}\left(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_P\right)\right)\chi_n\left(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_P\right) = E_{BO}\ \chi_n\left(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_P\right) \tag{32}$$

4. Let $\Psi\left(\boldsymbol{r}_1,\sigma_1;\boldsymbol{r}_2,\sigma_2;\ldots;\boldsymbol{r}_N,\sigma_N\right)$ be antisymmetric with respect to exchange of any two electronic coordinates. Show that the probability of two electrons with the same spin being at the same location is zero.

The wave function is antisymmetric with respect to simultaneous exchange of space and spin coordinates, so

$$\Psi\left(\boldsymbol{r}_1,\sigma_1;\boldsymbol{r}_2,\sigma_2;\ldots;\boldsymbol{r}_N,\sigma_N\right)=-\Psi\left(\boldsymbol{r}_2,\sigma_2;\boldsymbol{r}_1,\sigma_1;\ldots;\boldsymbol{r}_N,\sigma_N\right)$$

If $\boldsymbol{r}_1=\boldsymbol{r}_2$ and $\sigma_1=\sigma_2$, then

$$\begin{aligned}\Psi\left(\boldsymbol{r}_1,\sigma_1;\boldsymbol{r}_1,\sigma_1;\ldots;\boldsymbol{r}_N,\sigma_N\right)&=-\Psi\left(\boldsymbol{r}_1,\sigma_1;\boldsymbol{r}_1,\sigma_1;\ldots;\boldsymbol{r}_N,\sigma_N\right)\\ 2\Psi\left(\boldsymbol{r}_1,\sigma_1;\boldsymbol{r}_1,\sigma_1;\ldots;\boldsymbol{r}_N,\sigma_N\right)&=0\\ \Psi\left(\boldsymbol{r}_1,\sigma_1;\boldsymbol{r}_1,\sigma_1;\ldots;\boldsymbol{r}_N,\sigma_N\right)&=0\end{aligned}$$

Then

$$\left|\Psi\left(\boldsymbol{r}_1,\sigma_1;\boldsymbol{r}_1,\sigma_1;\ldots;\boldsymbol{r}_N,\sigma_N\right)\right|^2=0$$

5. Which of the following statements are true.

(a) A Bohr is about .5 Angstroms.

(b) An Angstrom is about .5 Bohr.

(c) A Hartree is about 27 electron volts.

(d) An electron volt is about 27 Hartree.

(e) A Hartree is about 2,200 cm^{-1}.

(f) An cm^{-1} is about 2,200 Hartree.

(g) A Hartree is about 2,600 kJ/mol.

(h) A kJ/mol is about 2600 Hartree.

6. Write the <u>radial</u> Schrödinger Equation for the one-electron atom with atomic number Z and orbital angular momentum quantum number l <u>in atomic units</u>.

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{l(l+1)}{2r^2}-\frac{Z}{r}\right)R_{n,l}(r)=E\ R_{n,l}(r)$$

In particle physics experiments, one often observes "exotic" atoms, where two particles bind to each other to form a hydrogen-like atom. In problems seven and eight, let's imagine an atom where the electron, e^-, was replaced by an antimuon, μ^+. The antimuon has a charge of $+e$ (where e is the magnitude of the charge of the electron) and a mass that is 203 times the mass of the electron. According to the standard model of particle physics, the heaviest baryon (the proton is the lightest baryon) will have the quark configuration $(\mathrm{ttb})^+$, with mass about 700,000 times that of the electron. (By contrast, the mass of the proton is 1836 times that of the electron.) This "heavy baryon," which has not yet been observed experimentally, could be called the "top proton" (because it is similar to the normal proton, but with up and down quarks replaced by top and bottom quarks). The anti-top proton, $\overline{(ttb)}$ has a charge equal to that of the electron (-e), and the same mass as the "top proton." Summarizing, then, we have:

	Hydrogen Atom		Exotic "anti-top muon" hydrogen-like atom.	
particles	electron (e^-)	proton (p)	antimuon (μ^+)	anti-"top proton" $\overline{(ttb)}$
charge	$-e$	$+e$	$+e$	$-e$
mass	m_e	1836 m_e	203 m_e	$698,000\ m_e$

For the purposes of questions seven and eight, ignore the effects of nuclear forces; we are only interested in the electrostatic interaction between the light particle (the electron or the antimuon) and the heavy particle (the proton or the anti-top proton).

7. Using the Born-Oppenheimer Approximation, the ground-state electrostatic energy of the exotic "anti-top muon" hydrogen-like atom is:

$$E_{\substack{\text{anti-top muon}\\ \text{exotic atom}}} = \underline{\quad \frac{-203}{2} \quad} \text{ Hartree}$$

8. The Born-Oppenheimer approximation is

(a) more accurate for the hydrogen atom than for the exotic "anti-top muon" hydrogen-like atom.

(b) less accurate for the hydrogen atom than for the exotic "anti-top muon" hydrogen-like atom. *[NOTE: This is true because the muon is "slow" compared to the anti-top proton. If it was not true that* $\frac{203 m_e}{698,000 m_e} < \frac{1}{1836 m_e}$ *then this* <u>*would not*</u> *be true, and the answer would be (a).]*

Usually the form of the wave function for a hydrogen-like atom is a rather complicated function of *r*, θ, and ϕ. However, for certain special values of the principle quantum number, *n*, and orbital angular momentum quantum number, *l*, the wave function takes a simple form. In problems 9 and 10, we will consider the lowest-energy *g*-orbital.

9. For the one-electron atom with atomic number *Z*, the lowest-energy *g* orbital is proportional to

$$\psi_{\substack{\text{lowest energy}\\ \text{g orbital}}}(r,\theta,\phi) \propto r^4 e^{-\left(\frac{Z}{5}\right)r} Y_4^m(\theta,\phi) \qquad (m = -4,-3,-2,\ldots 4)$$

10. The energy of the lowest-energy *g* orbital is (in atomic units):

$$E_{\substack{\text{lowest energy}\\ \text{g orbital}}} = -\frac{Z^2}{2\left(5^2\right)} \quad \text{Hartree}$$

$$= -\frac{Z^2}{50} \quad \text{Hartree}$$

11-12. For each of the following orbitals, write the appropriate eigenvalue. (If the orbital is not an eigenvalue of the operator in question, write "not an eigenvalue" (or something similar) to indicate this.)

$$\hat{L}^2 \; \psi_{2p_x}(\boldsymbol{r}) = 2 \; \psi_{2p_x}(\boldsymbol{r}) \quad \left(\text{in atomic units with } \hbar = m_e = 1\right)$$

$$\hat{L}^2 \; \psi_{3d_{3z^2-r^2}}(\boldsymbol{r}) = 6 \; \psi_{3d_{3z^2-r^2}}(\boldsymbol{r})$$

$$\hat{L}_z \; \psi_{2p_x}(\boldsymbol{r}) = \left[\text{not an eigenfunction of } \hat{L}_z\right] \quad \psi_{2p_x}(\boldsymbol{r})$$

$$\hat{L}_z \; \psi_{3d_{3z^2-r^2}}(\boldsymbol{r}) = 0 \cdot \psi_{3d_{3z^2-r^2}}(\boldsymbol{r}) = 0$$

13-14. The following statements pertain to the restricted-Hartree-Fock method (RHF) and the unrestricted Hartree-Fock method (UHF). Which of the following statements are true?

(a) The Hartree-Fock method includes the effects of electron correlation.

(b) The RHF wave function is usually chosen to be an eigenfunction of $\hat{S}^2$ and $\hat{L}^2$.

(c) The UHF wave function is usually chosen to be an eigenfunction of $\hat{S}^2$ and $\hat{L}^2$.

(d) In an RHF wave function, α -spin electrons and β -spin electrons occupy the same "spatial" orbitals.

(e) In an UHF wave function, α -spin electrons and β -spin electrons occupy the same "spatial" orbitals.

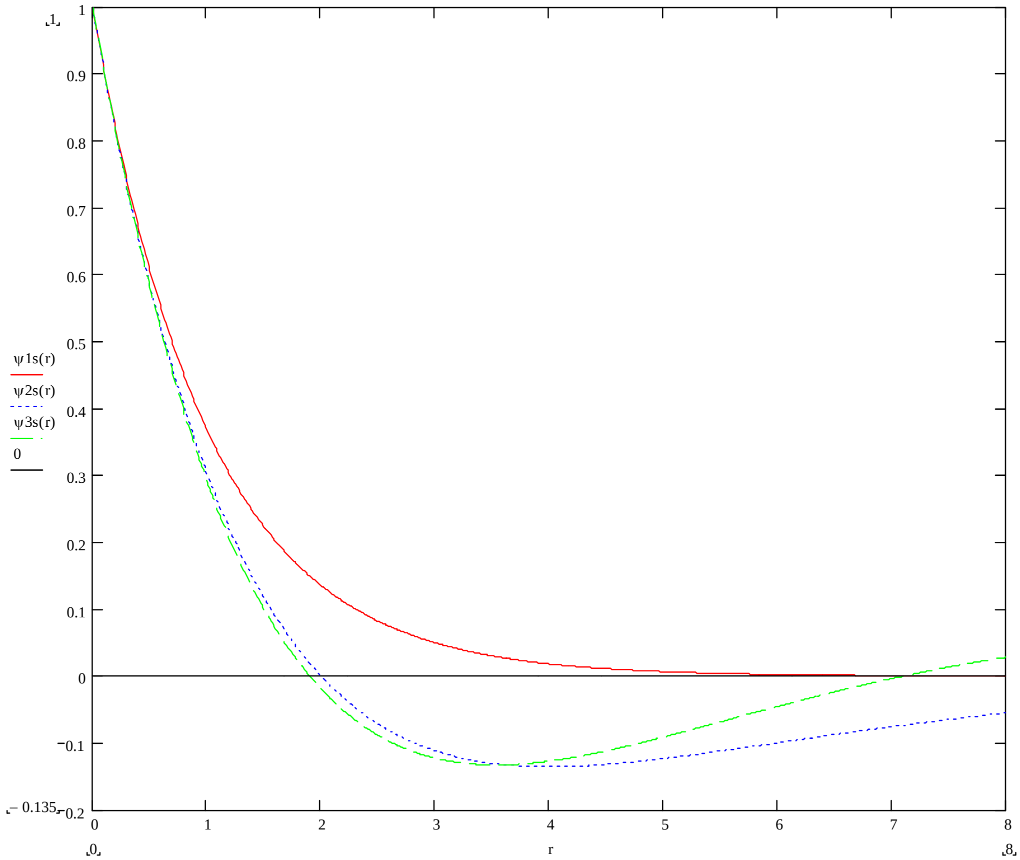
(f) The UHF wave function is higher in energy than the RHF wave function.

(g) The RHF wave function is higher in energy than the UHF wave function.

(h) The RHF energy is greater than the exact energy.

(i) The UHF energy is greater than the exact energy.

15. Below, <u>sketch</u> the 1s, 2s, and 3s orbitals in the Hydrogen atom.



As a very primitive model of the Helium atom, we computed the energy of the atom when we neglected the electron-electron repulsion entirely, obtaining an energy of -4 Hartree.

16. Neglecting electron-electron repulsion, what is the energy of the Neon atom? (Write your answer in Hartree units.)

In this case, the energy would be the sum of the orbital energies in the one-electron atom. So

$$\begin{aligned} E_{\substack{\text{no e-e}\\ \text{repulsion}}} &= (2\text{ electrons})(1\text{s orbital energy}) + (2\text{ electrons})(2\text{s orbital energy}) \\ &\quad + (6\text{ electrons})(2\text{p orbital energy}) \\ &= (2)\left(-\frac{(10)^2}{2}\right) + 2\left(\frac{-(10)^2}{2(2^2)}\right) + 6\left(\frac{-(10)^2}{2(2^2)}\right) \\ &= (10)^2\left(-1-\tfrac{1}{4}-\tfrac{3}{4}\right) \\ &= -200\text{ Hartree} \end{aligned} \tag{33}$$

The actual energy is about -128 Hartree.

17. The answer in question 16 is

(a) less than the exact ground-state energy of the Neon atom.

(b) greater than the exact ground-state energy of the Neon atom.

18. Write an appropriate Slater determinant (include all the rows and all the columns) for a ^3S state with the $1s^2 2s^1 5s^1$ electron configuration. Remember to include the appropriate normalization constant for orthogonal and normalized orbitals.

$$\Psi_{1s^2 2s^1 5s^1} = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_{1s}(\boldsymbol{r}_1)\alpha(1) & \psi_{1s}(\boldsymbol{r}_1)\beta(1) & \psi_{2s}(\boldsymbol{r}_1)\alpha(1) & \psi_{5s}(\boldsymbol{r}_1)\alpha(1) \\ \psi_{1s}(\boldsymbol{r}_2)\alpha(2) & \psi_{1s}(\boldsymbol{r}_2)\beta(2) & \psi_{2s}(\boldsymbol{r}_2)\alpha(2) & \psi_{5s}(\boldsymbol{r}_2)\alpha(2) \\ \psi_{1s}(\boldsymbol{r}_3)\alpha(3) & \psi_{1s}(\boldsymbol{r}_3)\beta(3) & \psi_{2s}(\boldsymbol{r}_3)\alpha(3) & \psi_{5s}(\boldsymbol{r}_3)\alpha(3) \\ \psi_{1s}(\boldsymbol{r}_4)\alpha(4) & \psi_{1s}(\boldsymbol{r}_4)\beta(4) & \psi_{2s}(\boldsymbol{r}_4)\alpha(4) & \psi_{5s}(\boldsymbol{r}_4)\alpha(4) \end{vmatrix}$$

Name:

	M_L					
M_S	**5**	**4**	**3**	**2**	**1**	**0**
3/2			$\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_1}\alpha\ \ \psi_{3d_0}\alpha\right\|$	$\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_1}\alpha\ \ \psi_{3d_{-1}}\alpha\right\|$	$\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_1}\alpha\ \ \psi_{3d_{-2}}\alpha\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_{-1}}\alpha\right\|$	$\left\|\psi_{3d_1}\alpha\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_{-1}}\alpha\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_{-2}}\alpha\right\|$
1/2	$\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_2}\beta\ \ \psi_{3d_1}\alpha\right\|$	$\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_1}\alpha\ \ \psi_{3d_1}\beta\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_2}\beta\ \ \psi_{3d_0}\alpha\right\|$	$\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_1}\alpha\ \ \psi_{3d_0}\beta\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_1}\beta\ \ \psi_{3d_0}\alpha\right\|$ $\left\|\psi_{3d_2}\beta\ \ \psi_{3d_1}\alpha\ \ \psi_{3d_0}\alpha\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_2}\beta\ \ \psi_{3d_{-1}}\alpha\right\|$	$\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_1}\alpha\ \ \psi_{3d_{-1}}\beta\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_1}\beta\ \ \psi_{3d_{-1}}\alpha\right\|$ $\left\|\psi_{3d_2}\beta\ \ \psi_{3d_1}\alpha\ \ \psi_{3d_{-1}}\alpha\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_2}\beta\ \ \psi_{3d_{-2}}\alpha\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_0}\beta\right\|$ $\left\|\psi_{3d_1}\alpha\ \ \psi_{3d_1}\beta\ \ \psi_{3d_0}\alpha\right\|$	$\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_1}\alpha\ \ \psi_{3d_{-2}}\beta\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_1}\beta\ \ \psi_{3d_{-2}}\alpha\right\|$ $\left\|\psi_{3d_2}\beta\ \ \psi_{3d_1}\alpha\ \ \psi_{3d_{-2}}\alpha\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_{-1}}\beta\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_0}\beta\ \ \psi_{3d_{-1}}\alpha\right\|$ $\left\|\psi_{3d_2}\beta\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_{-1}}\alpha\right\|$ $\left\|\psi_{3d_1}\alpha\ \ \psi_{3d_1}\beta\ \ \psi_{3d_{-1}}\alpha\right\|$ $\left\|\psi_{3d_1}\alpha\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_0}\beta\right\|$	$\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_{-2}}\beta\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_0}\beta\ \ \psi_{3d_{-2}}\alpha\right\|$ $\left\|\psi_{3d_2}\beta\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_{-2}}\alpha\right\|$ $\left\|\psi_{3d_1}\alpha\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_{-1}}\beta\right\|$ $\left\|\psi_{3d_1}\alpha\ \ \psi_{3d_0}\beta\ \ \psi_{3d_{-1}}\alpha\right\|$ $\left\|\psi_{3d_1}\beta\ \ \psi_{3d_0}\alpha\ \ \psi_{3d_{-1}}\alpha\right\|$ $\left\|\psi_{3d_1}\alpha\ \ \psi_{3d_1}\beta\ \ \psi_{3d_{-2}}\alpha\right\|$ $\left\|\psi_{3d_2}\alpha\ \ \psi_{3d_{-1}}\alpha\ \ \psi_{3d_{-1}}\beta\right\|$

19. List all the terms associated with the ground state electron configuration of Vanadium, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$. (You do not need to show the possible values of *J* here.)

^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D, ^2P

20. What is the term symbol for the ground state term of the Cobalt atom, which has electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$?

This is the same as the Vanadium case, but in this case we are dealing with "holes" instead of electrons. So the ground state term symbol is ^4F. *However*, the best value of $J = L + S = 3 + \frac{3}{2} = \frac{9}{2}$ because in this case the shell is more than half-filled. (For Vanadium the best value of $J = |L - S| = |3 - \frac{3}{2}| = \frac{3}{2}$). So the ground state term symbol is $^4F_{9/2}$.

Name:

21. What are the possible values of M_J in the ground state of the Cobalt atom?

$M_J = -\frac{9}{2}, -\frac{7}{2}, -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$

22. We are interested in the $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3 4p^1$ excited state of the Manganese atom. What are the possible terms?

There are a slew of different values—I should have counted the states before assigning this problem!

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ **Term**	**New range of L and S**	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3 4p^1$ **Term**
${}^4F$	$2 \le L \le 4; 1 \le S \le 2$	${}^5D, {}^5F, {}^5G; {}^3D, {}^3F, {}^3G$
${}^4P$	$0 \le L \le 2; 1 \le S \le 2$	${}^5S, {}^5P, {}^5D; {}^3S, {}^3P, {}^3D$
${}^2H$	$4 \le L \le 6; 0 \le S \le 1$	${}^3I, {}^3H, {}^3G; {}^1I, {}^1H, {}^1G$
${}^2G$	$3 \le L \le 5; 0 \le S \le 1$	${}^3F, {}^3H, {}^3G; {}^1F, {}^1H, {}^1G$
${}^2F$	$2 \le L \le 4; 0 \le S \le 1$	${}^3F, {}^3D, {}^3G; {}^1F, {}^1D, {}^1G$
${}^2D$	$1 \le L \le 3; 0 \le S \le 1$	${}^3F, {}^3D, {}^3P; {}^1F, {}^1D, {}^1P$
${}^2D$	$1 \le L \le 3; 0 \le S \le 1$	${}^3F, {}^3D, {}^3P; {}^1F, {}^1D, {}^1P$
${}^2P$	$0 \le L \le 2; 0 \le S \le 1$	${}^3D, {}^3P, {}^3S; {}^1D, {}^1P, {}^1S$

For each of the following, write the eigenvalue. (If there is no eigenvalue, write "no eigenvalue"; if there are multiple eigenvalues possible, write all the possibilities.) Here, the wave functions are denoted either by (a) a Slater determinant or (b) a term symbol. In each case, it is up to you to decipher the relevant quantum numbers.

23.

$$\hat{L}^2 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right| = 12 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right|$$

$$\hat{L}_z \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right| = 3 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right|$$

$$\hat{L}^2 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right| = \begin{bmatrix}\text{not an eigenfunction} \\ \text{of } \hat{L}^2\end{bmatrix} \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right|$$

$$\hat{L}_z \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right| = 4 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right|$$

24.

$$\hat{S}^2 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right| = \tfrac{15}{4} \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right|$$

$$\hat{S}_z \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right| = \tfrac{3}{2} \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right|$$

$$\hat{S}^2 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right| = \tfrac{3}{4} \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right|$$

$$\hat{S}_z \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right| = \tfrac{1}{2} \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right|$$

25.

$$\hat{J}^2 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right| = \begin{bmatrix}\text{not an eigenfunction since} \\ \left[\hat{J}^2, L_z\right] \neq 0; \left[\hat{J}^2, S_z\right] \neq 0\end{bmatrix} \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right|$$

$$\hat{J}_z \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right| = \left(3 + \tfrac{3}{2}\right)\left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right|$$

$$= \tfrac{9}{2}\left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right|$$

$$\hat{J}^2 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right| = \begin{bmatrix}\text{not an eigenfunction since} \\ \left[\hat{J}^2, L_z\right] \neq 0; \left[\hat{J}^2, S_z\right] \neq 0\end{bmatrix} \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right|$$

$$\hat{J}_z \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right| = \left(4 + \tfrac{1}{2}\right)\left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right|$$

$$= \left(\tfrac{9}{2}\right)\left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right|$$

Part 3. Closed-Book Derivation

1. Explain why $\hat{J}^2$ and $\hat{S}^2$ commute (7 points), but $\hat{J}^2$ and $\hat{S}_x$ do not (7 points).

You cannot use results for commutators including $\hat{\boldsymbol{J}}$; that is the purpose of this problem! Rather, you must rewrite terms containing $\hat{\boldsymbol{J}}$ in terms of $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$, and then use commutator identities (e.g., formulae for $\left[\hat{A},\hat{B}\hat{C}\right]$, $\left[\hat{A}\hat{B},\hat{C}\right]$, $\left[\hat{A},\hat{B}+\hat{C}\right]$, $\left[\hat{A}+\hat{B},\hat{C}\right]$) and known commutator relationships for the orbital angular momentum ($\hat{\boldsymbol{L}}=\left[\hat{L}_x,\hat{L}_y,\hat{L}_z\right]$, $\hat{L}^2=\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{L}}$) and the spin angular momentum ($\hat{\boldsymbol{S}}=\left[\hat{S}_x,\hat{S}_y,\hat{S}_z\right]$, $\hat{S}^2=\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{S}}$) or electrons to get the desired result.

You may find it helpful to recall that $\left[\hat{S}_x,\hat{S}_y\right]=i\hbar\hat{S}_z$, $\left[\hat{S}_y,\hat{S}_z\right]=i\hbar\hat{S}_x$, and $\left[\hat{S}_z,\hat{S}_x\right]=i\hbar\hat{S}_y$.

$$
\begin{aligned}
\left[\hat{J}^2,\hat{S}^2\right] &= \left[\hat{\boldsymbol{J}}\cdot\boldsymbol{J},\hat{S}^2\right] \\
&= \left[\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right)\cdot\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right),\hat{S}^2\right] \\
&= \left[\hat{L}^2+\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}}+\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}+\hat{S}^2,\hat{S}^2\right] \\
&= \left[\hat{L}^2+2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}}+\hat{S}^2,\hat{S}^2\right] && \begin{pmatrix}\text{because spin and orbital angular} \\ \text{momenta commute}\end{pmatrix} \\
&= \left[\hat{L}^2,\hat{S}^2\right]+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}^2\right]+\left[\hat{S}^2,\hat{S}^2\right] && \begin{pmatrix}\text{because the commutator of a sum} \\ \text{is the sum of the commutators}\end{pmatrix} \\
&= 0+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}^2\right]+\left[\hat{S}^2,\hat{S}^2\right] && (L \text{ and } S \text{ are both good quantum numbers!}) \\
&= 0+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}^2\right]+0 && (\text{every operator commutes with itself}) \\
&= 2\hat{\boldsymbol{S}}\cdot\left[\hat{\boldsymbol{L}},\hat{S}^2\right]+2\left[\hat{\boldsymbol{S}},\hat{S}^2\right]\cdot\hat{\boldsymbol{L}} && (\text{use identity for the commutator of a product}) \\
&= 0+2\left[\hat{\boldsymbol{S}},\hat{S}^2\right]\cdot\hat{\boldsymbol{L}} && \begin{pmatrix}\text{because spin and orbital angular} \\ \text{momenta commute}\end{pmatrix} \\
&= 2\left[\hat{S}_x,\hat{S}^2\right]\hat{L}_x+2\left[\hat{S}_y,\hat{S}^2\right]\hat{L}_y && (\text{definition of the dot product}) \\
&\quad +2\left[\hat{S}_z,\hat{S}^2\right]\hat{L}_z \\
&= 2(0)\hat{L}_x+2(0)\hat{L}_y+2(0)\hat{L}_z && \begin{pmatrix}\hat{S}^2 \text{ commutes with every component of the spin} \\ \text{angular momentum}\end{pmatrix} \\
&= 0
\end{aligned}
$$

$$
\begin{aligned}
\left[\hat{J}^2,\hat{S}_x\right] &= \left[\hat{\boldsymbol{J}}\cdot\boldsymbol{J},\hat{S}_x\right] \\
&= \left[\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right)\cdot\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right),\hat{S}_x\right] \\
&= \left[\hat{L}^2+\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}}+\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}+\hat{S}^2,\hat{S}_x\right] \\
&= \left[\hat{L}^2+2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}}+\hat{S}^2,\hat{S}_x\right] && \begin{pmatrix}\text{because spin and orbital angular}\\ \text{momenta commute}\end{pmatrix} \\
&= \left[\hat{L}^2,\hat{S}_x\right]+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}_x\right]+\left[\hat{S}^2,\hat{S}_x\right] && \begin{pmatrix}\text{because the commutator of a sum}\\ \text{is the sum of the commutators}\end{pmatrix} \\
&= 0+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}_x\right]+\left[\hat{S}^2,\hat{S}_x\right] && (L \text{ and } S \text{ are both good quantum numbers!}) \\
&= 0+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}_x\right]+0 && \begin{pmatrix}\hat{S}^2 \text{ commutes with every component of the spin}\\ \text{angular momentum}\end{pmatrix} \\
&= 2\hat{\boldsymbol{S}}\cdot\left[\hat{\boldsymbol{L}},\hat{S}_x\right]+2\left[\hat{\boldsymbol{S}},\hat{S}_x\right]\cdot\hat{\boldsymbol{L}} && (\text{use identity for the commutator of a product}) \\
&= 0+2\left[\hat{\boldsymbol{S}},\hat{S}_x\right]\cdot\hat{\boldsymbol{L}} && \begin{pmatrix}\text{because spin and orbital angular}\\ \text{momenta commute}\end{pmatrix} \\
&= 2\left[\hat{S}_x,\hat{S}_x\right]\hat{L}_x+2\left[\hat{S}_y,\hat{S}_x\right]\hat{L}_y && (\text{definition of the dot product}) \\
&\quad +2\left[\hat{S}_z,\hat{S}_x\right]\hat{L}_z \\
&= 0+2\left[\hat{S}_y,\hat{S}_x\right]\hat{L}_y \qquad +2\left[\hat{S}_z,\hat{S}_x\right]\hat{L}_z && (\text{every operator commutes with itself}) \\
&= 2\left(-i\hbar\hat{S}_z\right)\hat{L}_y \qquad +2\left(i\hbar\hat{S}_y\right)\hat{L}_z && \begin{pmatrix}\left[\hat{S}_x,\hat{S}_y\right]=i\hbar\hat{S}_z \rightarrow \left[\hat{S}_y,\hat{S}_x\right]=-i\hbar\hat{S}_z\\ \left[\hat{S}_z,\hat{S}_x\right]=i\hbar\hat{S}_y\end{pmatrix} \\
&= 2i\hbar\left(\hat{S}_y\hat{L}_z-\hat{S}_z\hat{L}_y\right) \\
&\neq 0
\end{aligned}
$$

Let $\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r) Y_l^m(\theta,\phi)$ denote the hydrogenic orbital ($Z=1$) with principle quantum number *n*, orbital angular momentum quantum number *l*, and magnetic quantum number *m*.

2a. (10 points) Show that

$$\left\langle \psi_{n,l,m} \left| \frac{1}{r} \right| \psi_{n,l,m} \right\rangle = \frac{1}{n^2}.$$

Write the general Hamiltonian for the one-electron atom,

$$\hat{H} = -\tfrac{\nabla^2}{2} - \tfrac{Z}{r} \tag{34}$$

Use the Hellmann-Feynman Theorem,

$$\begin{aligned}
\left.\frac{\partial E}{\partial Z}\right|_{Z=1} &= \left\langle \psi_{n,l,m}(\boldsymbol{r}) \left| \left.\frac{\partial \hat{H}}{\partial Z}\right|_{Z=1} \right| \psi_{n,l,m}(\boldsymbol{r}) \right\rangle \\
\left.\frac{\partial E}{\partial Z}\right|_{Z=1} &= \left\langle \psi_{n,l,m}(\boldsymbol{r}) \left| \tfrac{-1}{r} \right| \psi_{n,l,m}(\boldsymbol{r}) \right\rangle \\
\left.\frac{\partial E}{\partial Z}\right|_{Z=1} &= -\left\langle \psi_{n,l,m}(\boldsymbol{r}) \left| \tfrac{1}{r} \right| \psi_{n,l,m}(\boldsymbol{r}) \right\rangle
\end{aligned} \tag{35}$$

But, from the energy of the one-electron atom, we know that

$$\left.\frac{\partial E}{\partial Z}\right|_{Z=1} = \left.\frac{\partial\left(\frac{-Z^2}{2n^2}\right)}{\partial Z}\right|_{Z=1} = \left.\frac{-2Z}{2n^2}\right|_{Z=1} = -\frac{1}{n^2} \tag{36}$$

Substituting into Eq. (35) we get

$$\begin{aligned}
-\frac{1}{n^2} &= -\left\langle \psi_{n,l,m} \left| \frac{1}{r} \right| \psi_{n,l,m} \right\rangle \\
\frac{1}{n^2} &= \left\langle \psi_{n,l,m} \left| \frac{1}{r} \right| \psi_{n,l,m} \right\rangle
\end{aligned} \tag{37}$$

Kramer's relation is a very useful formula for computing integrals of the form $\langle \psi_{n,l,m} | r^k | \psi_{n,l,m} \rangle$ for one-electron atoms. When applied to the Hydrogen atom, Kramer's formula is:

$$\tfrac{k+1}{n^2}\langle \psi_{n,l,m} | r^k | \psi_{n,l,m} \rangle = (2k+1)\langle \psi_{n,l,m} | r^{k-1} | \psi_{n,l,m} \rangle + k\left[\tfrac{1}{4}(k^2-1) - l(l+1)\right]\langle \psi_{n,l,m} | r^{k-2} | \psi_{n,l,m} \rangle$$

2b. (6 points) What is the average (mean) distance from the nucleus of an electron in an *s* orbital of the hydrogen atom? Compare this to the result for *p* orbitals.

We need the formula with $k=1$, because we want to know the mean distance, which is given by the expression

$$\langle \psi_{n,l,m} | r | \psi_{n,l,m} \rangle = \text{mean distance} \tag{38}$$

We know

$$\langle \psi_{n,l,m} | r^{1-2} | \psi_{n,l,m} \rangle = \langle \psi_{n,l,m} | r^{-1} | \psi_{n,l,m} \rangle = \frac{1}{n^2} \tag{39}$$

from 2a. We know that

$$\langle \psi_{n,l,m} | r^{2-2} | \psi_{n,l,m} \rangle = \langle \psi_{n,l,m} | r^{0} | \psi_{n,l,m} \rangle = \langle \psi_{n,l,m} | \psi_{n,l,m} \rangle = 1 \tag{40}$$

because wave functions are normalized. So, we have that

$$\begin{aligned}
\tfrac{1+1}{n^2}\langle \psi_{n,l,m} | r^1 | \psi_{n,l,m} \rangle &= (2(1)+1)\langle \psi_{n,l,m} | r^0 | \psi_{n,l,m} \rangle \\
&\quad +1\left[\tfrac{1}{4}(1^2-1) - l(l+1)\right]\langle \psi_{n,l,m} | r^{-1} | \psi_{n,l,m} \rangle \\
\tfrac{2}{n^2}\langle \psi_{n,l,m} | r^1 | \psi_{n,l,m} \rangle &= 3 + 1\left[\tfrac{1}{4}(0) - l(l+1)\right]\frac{1}{n^2} \\
\langle \psi_{n,l,m} | r^1 | \psi_{n,l,m} \rangle &= \frac{1}{2}\left(3n^2 - l(l+1)\right)
\end{aligned} \tag{41}$$

For an s orbital, $l=0$ and so

$$\langle \psi_{n,0,0} | r^1 | \psi_{n,0,0} \rangle = \frac{1}{2}(3n^2) \tag{42}$$

while for a p orbital $l=1$ and so

$$\langle \psi_{n,1,m} | r^1 | \psi_{n,1,m} \rangle = \frac{1}{2}(3n^2-2) \tag{43}$$

Note that for a given value of the principle quantum number, n, an electron in a p orbital is actually closer, on average, to the nucleus than an electron in an s orbital.