

Short Answer Questions: (20 questions @ 3 points each = 60 points total).

Problems 1-4 are related to the Born-Oppenheimer approximation:

1. Write down the full Schrödinger equation for the Hydrogen molecule (H_2), including its dependence on the nuclear and electronic positions.

$$\left(\begin{array}{c} \text{nuclear kinetic energy} \quad \text{electronic kinetic energy} \quad \text{nuclear-nuclear repulsion} \quad \text{electron-electron repulsion} \\ -\frac{1}{2M_H}\nabla_{\mathbf{R}_A}^2 - \frac{1}{2M_H}\nabla_{\mathbf{R}_B}^2 - \frac{1}{2}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2}\nabla_{\mathbf{r}_2}^2 + \frac{1}{|\mathbf{R}_A - \mathbf{R}_B|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ \text{nuclear-electron attraction} \\ -\frac{1}{|\mathbf{r}_1 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|} \end{array} \right) \Psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_1, \mathbf{r}_2)$$

- 2,3. Using the Born-Oppenheimer approximation to simplify your result from #1, write down the *electronic* (#2) and *nuclear* (#3) Schrödinger equations for the Hydrogen molecule.

#2

$$\left(\begin{array}{c} \text{electronic kinetic energy} \quad \text{nuclear-nuclear repulsion} \quad \text{electron-electron repulsion} \\ -\frac{1}{2}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2}\nabla_{\mathbf{r}_2}^2 + \frac{1}{|\mathbf{R}_A - \mathbf{R}_B|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ \text{nuclear-electron attraction} \\ -\frac{1}{|\mathbf{r}_1 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|} \end{array} \right) \Psi_{el}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_A, \mathbf{R}_B) = U(\mathbf{R}_A, \mathbf{R}_B) \Psi_{el}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_A, \mathbf{R}_B)$$

#3.
$$\left(\begin{array}{c} \text{nuclear kinetic energy} \quad \text{potential energy surface} \\ -\frac{1}{2M_H}\nabla_{\mathbf{R}_A}^2 - \frac{1}{2M_H}\nabla_{\mathbf{R}_B}^2 + U(\mathbf{R}_A, \mathbf{R}_B) \end{array} \right) \chi_{\text{nucl}}(\mathbf{R}_A, \mathbf{R}_B) = E\chi_{\text{nucl}}(\mathbf{R}_A, \mathbf{R}_B)$$

4. For which of the following molecules will the Born-Oppenheimer be *least* accurate.

(a) SiO_4

(b) I_2
(c) UF_6

(d) PCl_3

5. Suppose you are given a hydrogen atom in its ground state, and you take the spectrum of the atom. Assuming the laser is weak enough so that only electric dipole transitions are possible, to which of the following excited states is a transition allowed?

(a) $^1S_{1/2}$
(b) $^2S_{1/2}$
(c) $^3S_{1/2}$

(d) $^2P_{1/2}$
(e) $^2P_{3/2}$
(f) $^1P_{1/2}$

(g) $^2D_{1/2}$
(h) $^2D_{3/2}$
(i) $^2D_{5/2}$
(j) $^2F_{1/2}$

(k) $^2F_{3/2}$
(l) $^2F_{5/2}$

6. The wavefunctions of the hydrogen atom are usually written in terms of which of the following “special functions.” (There may be multiple answers.)

- | | |
|--|--|
| (a) Jacobi polynomials | (f) associated Schrödinger polynomials |
| (b) Dirac polynomials | (h) associated Jacobi polynomials |
| (c) Hartree harmonics | (i) Hermite functions |
| (d) Poincare polynomials | (j) spherical harmonics |
| (e) associated Laguerre polynomials | (h) Matthieu functions |

7. What is the wavelength of the lowest-energy excitation of an He^+ cation in its ground state.

The difference in energy between the lowest energy allowed excited state (2p) and the ground state (1s) is:

$$\Delta E_{2p \rightarrow 1s} = \frac{-(2)^2}{2(2)^2} - \left(\frac{-(2)^2}{2(1)^2} \right) = \frac{-4}{8} + \frac{4}{2} = \frac{3}{2} \text{ Hartree}$$

$\left(\begin{array}{l} \text{using } E_{nlm_l} = \frac{-Z^2}{2n^2} \\ \text{for one-electron} \\ \text{atoms and ions} \end{array} \right)$

Then, converting to SI units,

$$\Delta E_{2p \rightarrow 1s} = \frac{3}{2} \text{ Hartree} = \left(\frac{3}{2} \text{ Hartree} \right) \left(4.359 \cdot 10^{-18} \frac{\text{J}}{\text{Hartree}} \right)$$

$$= 6.5385 \cdot 10^{-18} \text{ J}$$

and using $E = h\nu = hc/\lambda$,

$$\Delta E_{2p \rightarrow 1s} = 6.5385 \cdot 10^{-18} \text{ J} = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{6.5385 \cdot 10^{-18} \text{ J}} = \frac{(6.6262 \cdot 10^{-34} \text{ J} \cdot \text{s}) (2.9979 \cdot 10^8 \frac{\text{m}}{\text{s}})}{6.5385 \cdot 10^{-18} \text{ J}}$$

$$= 3.038 \cdot 10^{-8} \text{ m}$$

$$= 30.38 \text{ nm}$$

8. Suppose you are given the following information about the wavefunction of the Li^{++} dication

- Very close to the nucleus, the wavefunction has the form r^4 .
- The orbital angular momentum around the z-axis is zero. (I.e., there is no orbital angular momentum around the z-axis.)
- Very far from the nucleus, the wavefunction decays exponentially like $\exp\left(-\frac{3}{5}r\right)$.

What type of orbital is this? (I.e., what are the values of the n , l , and m_l quantum numbers.)

Because near the nucleus the wavefunction looks like $r^l e^{-\frac{Zr}{n}}$ we have $l = 4$. This is a **g orbital**.

The orbital angular momentum around the z-axis is zero, which means $m_l = 0$.

The long-range decay of the wavefunction is controlled by the exponential,

$$e^{-r\sqrt{-2E}} = e^{-\left(\frac{Z}{n}\right)r} \text{ so } Z/n = 3/n = 3/5 \text{ and } n = 5. \text{ It is a } 5g_0 \text{ orbital.}$$

9. Is the following equation an appropriate approximation to the ground state wavefunction of the Helium atom?

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) \propto e^{-\zeta r_1} e^{-\zeta r_2} \left(1 + b|\mathbf{r}_1 - \mathbf{r}_2| + c|\mathbf{r}_1 - \mathbf{r}_2|^2 \right) [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

(a) yes

(b) no It is not antisymmetric!!

- 10,11. Write a Slater determinant wavefunction for the ground state of the Lithium atom (3 electrons). Be sure to (a) write out the determinant in the *long form*, showing all three rows and all three columns and (b) include the appropriate normalization factor.

$$\Psi_{Li} = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{1s}(\mathbf{r}_1)\alpha(1) & \phi_{1s}(\mathbf{r}_1)\beta(1) & \phi_{2s}(\mathbf{r}_1)\alpha(1) \\ \phi_{1s}(\mathbf{r}_2)\alpha(2) & \phi_{1s}(\mathbf{r}_2)\beta(2) & \phi_{2s}(\mathbf{r}_2)\alpha(2) \\ \phi_{1s}(\mathbf{r}_3)\alpha(3) & \phi_{1s}(\mathbf{r}_3)\beta(3) & \phi_{2s}(\mathbf{r}_3)\alpha(3) \end{vmatrix}$$

12. What are the term symbols associated with the ground-state electron configuration of the Cerium atom, $[\text{Xe}]6s^2 4f^1 5d^1$? You do not need to include the “ J labels.”

This is coupling two inequivalent terms, one with $L = 3, S = \frac{1}{2}$ ($4f^1$) and one with $L = 2, S = \frac{1}{2}$ ($5d^1$). The $6s^2$ is $L = 0, S = 0$ and does not contribute. The range of L and S are thus:

$$\begin{aligned} |L_{4f^1} - L_{5d^1}| &= |3 - 2| = 1 \leq L \leq 5 = |3 + 2| = |L_{4f^1} + L_{5d^1}| \\ |S_{4f^1} - S_{5d^1}| &= \left| \frac{1}{2} - \frac{1}{2} \right| = 0 \leq S \leq 1 = \left| \frac{1}{2} + \frac{1}{2} \right| = |S_{4f^1} + S_{5d^1}| \end{aligned}$$

Making all possible combinations of L and S then gives:

$$^1P, ^1D, ^1F, ^1G, ^1H$$

$$^3P, ^3D, ^3F, ^3G, ^3H$$

13. Consider an electron in the Argon atom ($N = Z = 18$). When an electron is very, very far from the Argon nucleus, it feels an effective nuclear charge of

$$Z_{eff} = \underline{\hspace{1cm}} \mathbf{1} \underline{\hspace{1cm}}$$

Very far away the atom sees the nucleus (+18 charge) screened by 17 electrons (17 times -1 charge).

14. The ground state of the Titanium atom ($[\text{Ar}]4s^2 3d^2$) is described by the 3F term symbol. What are the possible values of the total angular momentum quantum number, J , for associated with this 3F state?

$$|L - S| \leq J \leq L + S$$

$$|3 - 1| = 2 \leq J \leq 4 = 3 + 1$$

$$J = 2, 3, 4$$

15. Assuming that Hund's third rule holds, which of the values of J in #14 is associated with the state of lowest energy?

Since the subshell is less than half-filled, the lowest value of J is preferred. So $J = \underline{2}$.

16. Let $\Psi_{g.s.}^{Ti}$ denote the ground-state wavefunction for the Titanium atom (cf #14). What are the eigenvalue(s) of the following operators. When there are multiple possibilities, list all of them. Be sure to *explicitly show* the dependence on \hbar .

$$\hat{L}^2 \Psi_{g.s.}^{Ti} = \hbar^2 L(L+1) \Psi_{g.s.}^{Ti} = \hbar^2 (3(3+1)) \Psi_{g.s.}^{Ti} = 12\hbar^2 \Psi_{g.s.}^{Ti}$$

$$\hat{S}^2 \Psi_{g.s.}^{Ti} = \hbar^2 S(S+1) \Psi_{g.s.}^{Ti} = \hbar^2 1(2+1) \Psi_{g.s.}^{Ti} = 2\hbar^2 \Psi_{g.s.}^{Ti}$$

$$\hat{S}_z \Psi_{g.s.}^{Ti} = \hbar M_S \Psi_{g.s.}^{Ti} = (1, 0, \text{ or } -1) \hbar \Psi_{g.s.}^{Ti}$$

17. Using a linear combination of atomic orbitals (LCAO) is most closely associated with which of the following approaches to molecular quantum chemistry?

(a) molecular orbital theory | (b) valence bond theory

18. Using resonance structures to model electron pairing is most closely associated with which of the following approaches to molecular quantum chemistry?

(a) molecular orbital theory | (b) valence bond theory

The following text refers to problems 19 and 20.

Suppose you take the most general possible linear combinations of atomic orbitals,

$$\psi^{(j)}(\mathbf{r}) = \sum_{\alpha=1}^{N_{\text{atoms}}} \sum_{i=0}^{\infty} c_{\alpha i}^{(j)} \phi_{\alpha i}(\mathbf{r})$$

and then make a Slater determinant from these orbitals

$$\Psi = \begin{vmatrix} \psi^{(1)}\sigma_1 & \psi^{(2)}\sigma_2 & \cdots & \psi^{(N)}\sigma_N \end{vmatrix}$$

You then optimize the $c_{\alpha i}^{(j)}$ by minimizing the expectation value of the energy, $\langle E \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$.

19. What is the name of the computational method being described here?

Hartree-Fock

20. The energy obtained from the proposed computation is

(a) less than the exact ground-state energy for the system.

(b) equal to the exact ground-state energy for the system.

(c) greater than the exact ground-state energy for the system.

Problems

Pick THREE of the following five problems. **Clearly mark which problems you wish for me to grade. Cross out problems you do not wish me to grade.** If you do not mark which problems you wish to solve, I will mark the **first** three problems on which you have written **anything**. Each problem is worth 15 points. **Problems #1 and #5 have bonus portions which can be worked whether or not you choose to work on one of those problems.**

1. Variational Principles for excited states.

In class we learned about the variational principle for ground states. There are also versions of the variational principle for excited states. Let E_j and Ψ_j denote the energy eigenvalues and wavefunctions of a Hamiltonian, with $E_0 \leq E_1 \leq \dots$. So E_0 and Ψ_0 are the ground-state energy and wavefunction. Then the energy of the first excited state can be obtained by the revised variational principle:

The Conventional Variational Principle for the first excited state: Minimizing the expectation value of the energy with respect to all wavefunctions that are orthogonal to the ground-state wavefunction gives the energy of the first (lowest-energy) excited state. I.e.,

$$E_1 = \min_{\{\Psi | \langle \Psi | \Psi_0 \rangle = 0\}} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

1. Derive the variational principle for the first excited state. (15 pts.)

This problem is *very close* to the derivation of the “normal” variational principle for ground states. We start by expanding the wavefunction in terms of the eigenfunctions of the Hamiltonian;

$$\begin{aligned} \hat{H} |\Psi_k\rangle &= E_k |\Psi_k\rangle \\ |\Psi\rangle &= \sum_{k=0}^{\infty} c_k |\Psi_k\rangle \end{aligned}$$

The constraint that $\langle \Psi | \Psi_0 \rangle = 0$ restricts the wavefunction, and therefore the values of $\{c_k\}_{k=0}^{\infty}$ that can be used in its expansion. You could probably tell, by inspection, that the restriction on the $\{c_k\}_{k=0}^{\infty}$ is that $c_0 = 0$ (while $c_{k>0}$ is still arbitrary). But if you don't see this, you can derive it as follows:

$$0 = \langle \Psi | \Psi_0 \rangle = \left\langle \sum_{k=0}^{\infty} c_k \Psi_k \middle| \Psi_0 \right\rangle = \sum_{k=0}^{\infty} c_k \langle \Psi_k | \Psi_0 \rangle = \sum_{k=0}^{\infty} c_k \delta_{k0} = c_0$$

In any event, the constraint on the variational principle means that the wavefunctions that we are allowed to minimize over all have the form

$$|\Psi\rangle = \sum_{k=1}^{\infty} c_k |\Psi_k\rangle \quad \left(\text{sum now starts at } k=1 \text{ !!!}\right)$$

By just changing the lower index on the sum, the derivation in the notes works *exactly* the same way! We can do that derivation in several ways (we did two in class). One way is to write out the expectation value explicitly,

$$\begin{aligned}
\frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} &= \frac{\left\langle \sum_{k=1}^{\infty} c_k \Psi_k \left| \hat{H} \right| \sum_{l=1}^{\infty} c_l \Psi_l \right\rangle}{\left\langle \sum_{m=1}^{\infty} c_m \Psi_m \left| \sum_{n=1}^{\infty} c_n \Psi_n \right\rangle} = \frac{\sum_{k=1}^{\infty} \sum_{l=1}^{\infty} c_k^* c_l \langle \Psi_k | \hat{H} | \Psi_l \rangle}{\sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \langle \Psi_m | \Psi_n \rangle} = \frac{\sum_{k=1}^{\infty} \sum_{l=1}^{\infty} c_k^* c_l \langle \Psi_k | E_l | \Psi_l \rangle}{\sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \delta_{mn}} \\
&= \frac{\sum_{k=1}^{\infty} \sum_{l=1}^{\infty} c_k^* c_l E_l \delta_{kl}}{\sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \delta_{mn}} = \frac{\sum_{k=1}^{\infty} |c_k|^2 E_k}{\sum_{m=1}^{\infty} |c_m|^2} = \sum_{k=1}^{\infty} \left(\frac{|c_k|^2}{\sum_{m=1}^{\infty} |c_m|^2} \right) E_k
\end{aligned}$$

This is the equation for a weighted average of energies. Each term in the sum is positive, and the terms all add up to zero. That is, if you let p_k denote the probability of observing the state k , and so obviously

$$0 \leq p_k \leq 1 \quad 1 = \sum_{k=0}^{\infty} p_k$$

then you could rewrite this expression as

$$\frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \sum_{k=1}^{\infty} p_k E_k$$

OR

$$\frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \sum_{k=0}^{\infty} p_k E_k \quad (\text{with } p_0 = 0)$$

The choice of $\{p_k\}_{k=1}^{\infty}$ that gives the lowest energy is when the maximum probability (equal to one!) is for the lowest-energy state that is allowed. Since we order the states in increasing order,

$$E_0 \leq E_1 \leq E_2 \leq \dots$$

the lowest-energy state we can have in this case (since $c_0 = p_0 = 0$) is associated with $p_1 = 1; p_{k>1} = 0$. Thus $|c_1| = 1$ and $c_{k>1} = 0$. Looking back at the previous equations, it is clear that the energy at the minimum is the energy of the first excited-state

$$\begin{aligned}
\min_{\{\Psi | \langle \Psi | \Psi_0 \rangle = 0\}} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} &= \min_{\{\Psi | \langle \Psi | \Psi_0 \rangle = 0\}} \sum_{k=1}^{\infty} p_k E_k = \min_{\{\Psi | \langle \Psi | \Psi_0 \rangle = 0\}} \sum_{k=1}^{\infty} \left(\frac{|c_k|^2}{\sum_{m=1}^{\infty} |c_m|^2} \right) E_k \\
&\rightarrow |c_1|^2 E_1 = E_1
\end{aligned}$$

and the wavefunction at the minimum is the first-excited state wavefunction,

$$\sqrt{1} \Psi_1 \propto \Psi_1.$$

An alternative variational principle for the first excited state is called the Courant max-min principle. This is useful when the exact ground-state wavefunction is not known ahead of time.

Courant max-min principle: Minimizing the expectation value of the energy with respect to all wavefunctions that are orthogonal to some “trial” function, $\tilde{\Psi}$, and then maximizing the resulting “minimized trial energy” with respect to the choice of $\tilde{\Psi}$ gives the exact energy for the first excited state. Moreover, at the solution, $\tilde{\Psi}$ is the ground-state wavefunction. I.e.,

$$E_1 = \max_{\tilde{\Psi}} \min_{\{\Psi | \langle \Psi | \tilde{\Psi} \rangle = 0\}} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$\Psi_0 = \arg_{\tilde{\Psi}} \left(\max_{\tilde{\Psi}} \min_{\{\Psi | \langle \Psi | \tilde{\Psi} \rangle = 0\}} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right)$$

Bonus (5 pt): Derive the Courant max-min principle for the first excited state from the “conventional” excited-state variational principle in #1.

Notice that in the Courant max-min principle we are allowing the wavefunction to *vary*; since we are no longer *requiring* that $\tilde{\Psi} = \Psi_0$, the inner minimization is a “relaxation” of the constraint in “the Conventional Variational Principle for the first excited state” because now you are allowed to have a little bit of probability in the ground state. Relaxing a constraint always makes the minimum lower.¹ Anyway, based on this we have²

¹ There is a little subtlety here, but it is clear from the derivation of the previous result that if we had chose $\tilde{\Psi} = \Psi_{k>0}$, then the result of the variational principle would be E_0 and Ψ_0 . So we know that we have a variational principle that is bounded above.

² In fact, if $|\tilde{\Psi}\rangle = \sum_{k=0}^{\infty} \tilde{c}_k |\Psi_k\rangle$, it is not hard to show that the minimizing wavefunction in the

previous line is $|\Psi_{\min}\rangle = \left(\sqrt{\frac{|\tilde{c}_1|^2}{|\tilde{c}_0|^2 + |\tilde{c}_1|^2}} \right) |\Psi_0\rangle - \text{sgn}(\tilde{c}_0 \tilde{c}_1) \sqrt{\frac{|\tilde{c}_0|^2}{|\tilde{c}_0|^2 + |\tilde{c}_1|^2}} |\Psi_1\rangle$ [assuming that \tilde{c}_0

and \tilde{c}_1 are real, and that $|\tilde{c}_1| > 0$], and that the minimizing energy is

$$E_{\min} = \left(\frac{|\tilde{c}_1|^2}{|\tilde{c}_0|^2 + |\tilde{c}_1|^2} \right) E_0 + \left(\frac{|\tilde{c}_0|^2}{|\tilde{c}_0|^2 + |\tilde{c}_1|^2} \right) E_1 < E_1.$$

$$\min_{\{\Psi|\langle\Psi|\tilde{\Psi}\rangle=0\}} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \leq \min_{\{\Psi|\langle\Psi|\Psi_0\rangle=0\}} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = E_1$$

and so:

$$\max_{\tilde{\Psi}} \min_{\{\Psi|\langle\Psi|\tilde{\Psi}\rangle=0\}} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \min_{\{\Psi|\langle\Psi|\Psi_0\rangle=0\}} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = E_1$$

But we know that the equality holds when $\tilde{\Psi} = \Psi_0$. So if maximum is achieved for the ground-state wavefunction.

2. Molecular Orbital Theory + Configuration Interaction and Valence Bond Theory + Ionic Contributions.

2a. Write down the simple 1s-orbital-based “valence bond” wavefunction for the hydrogen molecule (H_2), including the ionic contribution. (3 pts.)

$$\Psi^{VB+ionic} \propto \left(c_{\text{cov}} \left(\psi_{1s}^{(A)}(\mathbf{r}_1) \psi_{1s}^{(B)}(\mathbf{r}_2) + \psi_{1s}^{(B)}(\mathbf{r}_1) \psi_{1s}^{(A)}(\mathbf{r}_2) \right) + c_{\text{ionic}} \left(\psi_{1s}^{(A)}(\mathbf{r}_1) \psi_{1s}^{(A)}(\mathbf{r}_2) + \psi_{1s}^{(B)}(\mathbf{r}_1) \psi_{1s}^{(B)}(\mathbf{r}_2) \right) \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

2b. Write down the simple 1s-orbital-based “molecular orbital” wavefunction for the hydrogen molecule including the configuration interaction with the state where both electrons are in in the antibonding orbital. (3 pts.)

$$\Psi^{MO+CI} \propto \left(c_{\text{bond}} \left(\psi_{1s}^{(A)}(\mathbf{r}_1) + \psi_{1s}^{(B)}(\mathbf{r}_1) \right) \left(\psi_{1s}^{(A)}(\mathbf{r}_2) + \psi_{1s}^{(B)}(\mathbf{r}_2) \right) + c_{\text{antibond}} \left(\psi_{1s}^{(A)}(\mathbf{r}_1) - \psi_{1s}^{(B)}(\mathbf{r}_1) \right) \left(\psi_{1s}^{(A)}(\mathbf{r}_2) - \psi_{1s}^{(B)}(\mathbf{r}_2) \right) \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

2c. Show that these two wavefunctions are equivalent. I.e., show that the coefficients of the bonding/antibonding configurations in molecular orbital theory can be derived in terms of the coefficients of the ionic/covalent contributions in valence bond theory. (9 pts)

$$\begin{aligned} \Psi^{MO+CI} &\propto \left(c_{\text{bond}} \left(\psi_{1s}^{(A)}(\mathbf{r}_1) + \psi_{1s}^{(B)}(\mathbf{r}_1) \right) \left(\psi_{1s}^{(A)}(\mathbf{r}_2) + \psi_{1s}^{(B)}(\mathbf{r}_2) \right) + c_{\text{antibond}} \left(\psi_{1s}^{(A)}(\mathbf{r}_1) - \psi_{1s}^{(B)}(\mathbf{r}_1) \right) \left(\psi_{1s}^{(A)}(\mathbf{r}_2) - \psi_{1s}^{(B)}(\mathbf{r}_2) \right) \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \\ &= \left(c_{\text{bond}} \left(\psi_{1s}^{(A)}(\mathbf{r}_1) \psi_{1s}^{(A)}(\mathbf{r}_2) + \psi_{1s}^{(B)}(\mathbf{r}_1) \psi_{1s}^{(B)}(\mathbf{r}_2) + \psi_{1s}^{(A)}(\mathbf{r}_1) \psi_{1s}^{(B)}(\mathbf{r}_2) + \psi_{1s}^{(B)}(\mathbf{r}_1) \psi_{1s}^{(A)}(\mathbf{r}_2) \right) + c_{\text{antibond}} \left(\psi_{1s}^{(A)}(\mathbf{r}_1) \psi_{1s}^{(A)}(\mathbf{r}_2) + \psi_{1s}^{(B)}(\mathbf{r}_1) \psi_{1s}^{(B)}(\mathbf{r}_2) - \psi_{1s}^{(A)}(\mathbf{r}_1) \psi_{1s}^{(B)}(\mathbf{r}_2) - \psi_{1s}^{(B)}(\mathbf{r}_1) \psi_{1s}^{(A)}(\mathbf{r}_2) \right) \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \\ &= \left((c_{\text{bond}} + c_{\text{antibond}}) \left(\psi_{1s}^{(A)}(\mathbf{r}_1) \psi_{1s}^{(A)}(\mathbf{r}_2) + \psi_{1s}^{(B)}(\mathbf{r}_1) \psi_{1s}^{(B)}(\mathbf{r}_2) \right) + (c_{\text{bond}} - c_{\text{antibond}}) \left(\psi_{1s}^{(A)}(\mathbf{r}_1) \psi_{1s}^{(B)}(\mathbf{r}_2) + \psi_{1s}^{(B)}(\mathbf{r}_1) \psi_{1s}^{(A)}(\mathbf{r}_2) \right) \right) (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \\ &\propto \Psi^{VB+ionic} \end{aligned}$$

Moreover,

$$c_{\text{ion}} = c_{\text{bond}} + c_{\text{antibond}}$$

$$c_{\text{cov}} = c_{\text{bond}} - c_{\text{antibond}}$$

3. Bonding and Antibonding orbitals.

Consider the simplest possible representation of the bonding and antibonding wavefunctions in the H_2^+ molecule,

$$\begin{aligned}\psi_{\text{bonding}}(\mathbf{r}) &\propto \phi_{1s}^A(\mathbf{r}) + \phi_{1s}^B(\mathbf{r}) \\ \psi_{\text{antibonding}}(\mathbf{r}) &\propto \phi_{1s}^A(\mathbf{r}) - \phi_{1s}^B(\mathbf{r})\end{aligned}$$

Here $\phi_{1s}^A(\mathbf{r})$ and $\phi_{1s}^B(\mathbf{r})$ denote the 1s-hydrogenic wavefunctions centered on atoms A and B , respectively. **Show that electron density accumulates in the region between the atoms in the bonding orbital and is depleted in the region between the atoms in the antibonding orbital by comparing the electron density of the bonding/antibonding wavefunctions,**

$$\begin{aligned}\rho_{\text{bonding}}(\mathbf{r}) &= |\psi_{\text{bonding}}(\mathbf{r})|^2 \\ \rho_{\text{antibonding}}(\mathbf{r}) &= |\psi_{\text{antibonding}}(\mathbf{r})|^2\end{aligned}$$

to the “classical” nonbonding density associated with noninteracting but overlapping hydrogen atoms,

$$\rho_{\text{non}}(\mathbf{r}) = \frac{1}{2} \left(|\phi_{1s}^A(\mathbf{r})|^2 + |\phi_{1s}^B(\mathbf{r})|^2 \right).$$

I.e., compute and analyze $\rho_{\text{bonding}}(\mathbf{r}) - \rho_{\text{non}}(\mathbf{r})$ and $\rho_{\text{antibonding}}(\mathbf{r}) - \rho_{\text{non}}(\mathbf{r})$. **(15 points)**

The density the bonding and antibonding states can be computed as

$$\rho_{\text{bonding/antibonding}}(\mathbf{r}) = \frac{|\psi_{\text{bonding/antibonding}}(\mathbf{r})|^2}{\int |\psi_{\text{bonding/antibonding}}(\mathbf{r})|^2 d\mathbf{r}}$$

We have to divide by the integral to maintain normalization. If we insert the equations for the bonding and antibonding orbitals, then we have

$$\begin{aligned}\rho_{\text{bonding/antibonding}}(\mathbf{r}) &= \frac{|\phi_{1s}^{(A)}(\mathbf{r}) \pm \phi_{1s}^{(B)}(\mathbf{r})|^2}{\int |\phi_{1s}^{(A)}(\mathbf{r}) \pm \phi_{1s}^{(B)}(\mathbf{r})|^2 d\mathbf{r}} \\ &= \frac{|\phi_{1s}^{(A)}(\mathbf{r})|^2 \pm 2\phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) + |\phi_{1s}^{(B)}(\mathbf{r})|^2}{\int \left(|\phi_{1s}^{(A)}(\mathbf{r})|^2 \pm 2\phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) + |\phi_{1s}^{(B)}(\mathbf{r})|^2 \right) d\mathbf{r}} \\ &= \frac{|\phi_{1s}^{(A)}(\mathbf{r})|^2 \pm 2\phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) + |\phi_{1s}^{(B)}(\mathbf{r})|^2}{1 \pm 2 \int \phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) d\mathbf{r} + 1}\end{aligned}$$

I have used the fact that the 1s-wavefunction is real to neglect complex conjugates. To simplify the notation, I will define an overlap integral

$$S = \int \phi_{1s}^{(A)}(\mathbf{r}) \phi_{1s}^{(B)}(\mathbf{r}) d\mathbf{r}$$

$$0 \leq S \leq 1$$

So that I can write:

$$\begin{aligned} \rho_{\text{bonding}}^{\text{antibonding}}(\mathbf{r}) &= \frac{\left| \phi_{1s}^{(A)}(\mathbf{r}) \right|^2 \pm 2\phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) + \left| \phi_{1s}^{(B)}(\mathbf{r}) \right|^2}{2 \pm 2S} \\ &= \frac{\rho_{\text{non}}(\mathbf{r}) \pm \phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r})}{1 \pm S} \end{aligned}$$

This is already enough to see the main effect. For the binding orbital you have an additional term that will be big in the region where the orbitals overlap. For the antibonding term you subtract a term that is big where the orbitals overlap, so that the density is actually zero at the bond midpoint. If you want to show this mathematically, then write:

$$\begin{aligned} \rho_{\text{bonding}}^{\text{antibonding}}(\mathbf{r}) - \rho_{\text{non}}(\mathbf{r}) &\equiv \frac{\rho_{\text{non}}(\mathbf{r}) \pm \phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r})}{1 \pm S} - \rho_{\text{non}}(\mathbf{r}) \\ &= \left(\rho_{\text{non}}(\mathbf{r}) \pm \phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) \right) (1 \mp S + S^2 \mp S^3 + S^4 \mp \dots) - \rho_{\text{non}}(\mathbf{r}) \\ &= \pm \phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) \mp S \left(\rho_{\text{non}}(\mathbf{r}) \pm \phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) \right) (1 \pm S + S^2 \pm S^3 \dots) \\ &= \pm \phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) \mp S \left(\rho_{\text{non}}(\mathbf{r}) \pm \phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) \right) (1 \pm S + S^2 \pm S^3 \dots) \\ &= \pm \left(\phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) + \frac{S}{1 \pm S} \left(\rho_{\text{non}}(\mathbf{r}) \pm \phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) \right) \right) \end{aligned}$$

I repeatedly used the binomial series to obtain this form. The largest term is the first one. I can write this form in an instructive form using the explicit equation for the 1s-orbital:

$$\begin{aligned} \rho_{\text{bonding}}^{\text{antibonding}}(\mathbf{r}) - \rho_{\text{non}}(\mathbf{r}) &= \pm \left(\phi_{1s}^{(A)}(\mathbf{r})\phi_{1s}^{(B)}(\mathbf{r}) \right) + \left(\text{terms that are smaller in the "bond"} \right) \\ &\approx \pm \frac{Z^3}{\pi} e^{-Z(r_A + r_B)} \end{aligned}$$

So for a bonding orbital we add a contribution to the electron density that is big "between the atoms" (where $r_A + r_B$ is small) and for an antibonding orbital we subtract a similar contribution. So electron density builds up between the atoms.

4. Term symbols.

A very low-lying excited state of the Cerium atom has the electron configuration $[\text{Xe}]6s^2 4f^2$.

4a. What term symbols correspond to this electron configuration. You do not need to show the total angular momentum quantum number, J . (12 points)

$M_L \setminus M_S$	$M_S = 1$	$M_S = 0$
$M_L = 6$ (3+3)		$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_3} \beta \end{array} \right $ unique
$M_L = 5$ (3+2)	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_2} \alpha \end{array} \right $ unique	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_2} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_3} \beta & \phi_{4f_2} \alpha \end{array} \right $
$M_L = 4$ (3+1) (2+2)	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_1} \alpha \end{array} \right $ unique	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_2} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_3} \beta & \phi_{4f_2} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \alpha & \phi_{4f_2} \beta \end{array} \right $
$M_L = 3$ (3+0) (2+1)	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_0} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \alpha & \phi_{4f_1} \alpha \end{array} \right $	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_0} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_3} \beta & \phi_{4f_0} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \alpha & \phi_{4f_1} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \beta & \phi_{4f_1} \alpha \end{array} \right $
$M_L = 2$ (3+-1) (2+0) (1+1)	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_{-1}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \alpha & \phi_{4f_0} \alpha \end{array} \right $	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_{-1}} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_3} \beta & \phi_{4f_{-1}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \alpha & \phi_{4f_0} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \beta & \phi_{4f_0} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_1} \alpha & \phi_{4f_1} \beta \end{array} \right $
$M_L = 1$ (3+-2) (2+-1) (1+0)	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_{-2}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \alpha & \phi_{4f_{-1}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_1} \alpha & \phi_{4f_0} \alpha \end{array} \right $	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_{-2}} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_3} \beta & \phi_{4f_{-2}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \alpha & \phi_{4f_{-1}} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \beta & \phi_{4f_{-1}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_1} \alpha & \phi_{4f_0} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_1} \beta & \phi_{4f_0} \alpha \end{array} \right $
$M_L = 0$ (3+-3) (2+-2) (1+-1) (0+0)	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_{-3}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \alpha & \phi_{4f_{-2}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_1} \alpha & \phi_{4f_{-1}} \alpha \end{array} \right $	$\left \begin{array}{cc} \phi_{4f_3} \alpha & \phi_{4f_{-3}} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_3} \beta & \phi_{4f_{-3}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \alpha & \phi_{4f_{-2}} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_2} \beta & \phi_{4f_{-2}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_1} \alpha & \phi_{4f_{-1}} \beta \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_1} \beta & \phi_{4f_{-1}} \alpha \end{array} \right $ $\left \begin{array}{cc} \phi_{4f_0} \alpha & \phi_{4f_0} \beta \end{array} \right $

^1I , ^3H , ^1G , ^3F , ^1D , ^3P , ^1S

4b. To which values for L , S , M_L , and M_S can you assign a unique Slater determinant?

(These Slater determinant will be an eigenfunction of \hat{L}^2 , \hat{S}^2 , \hat{L}_z , and \hat{S}_z .) (3 pts.)

These are given by the entries in the table that have only one Slater determinant. Entries with multiple Slater determinants are (arbitrarily!) assigned to different values of L and S depending on how you choose "which to cross out." So the only unique terms here are:

$$M_L = 6; M_S = 0; L = 6; S = 0$$

$$M_L = -6; M_S = 0; L = 6; S = 0 \quad (\text{not shown in the table, but present by symmetry})$$

$$M_L = 5; M_S = 1; L = 5; S = 1$$

$$M_L = 4; M_S = 1; L = 5; S = 1$$

$$M_L = -5; M_S = 1; L = 5; S = 1$$

$$M_L = 5; M_S = -1; L = 5; S = 1 \quad (\text{not shown in the table, but present by symmetry})$$

$$M_L = -5; M_S = -1; L = 5; S = 1$$

$$M_L = -4; M_S = 1; L = 5; S = 1$$

$$M_L = 4; M_S = -1; L = 5; S = 1 \quad (\text{not shown in the table, but present by symmetry})$$

$$M_L = -4; M_S = -1; L = 5; S = 1$$

5. Expectation values in the one-electron atom.

There are many different ways to measure the “average” distance of an electron from the nucleus in one-electron atoms. For example

- The mean distance of an electron from the nucleus, $r_{\text{mean}} = \langle r \rangle$.
- The root-mean-square (rms) distance of an electron from the nucleus, $r_{\text{rms}} = \sqrt{\langle r^2 \rangle}$.
- The most probable distance of an electron from the nucleus, r_{mp} .

You may find it helpful to recall that the $1s$ -wavefunction for a Hydrogen atom whose nucleus is at the origin is

$$\phi_{1s}(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi}} e^{-Zr}$$

The following integral may be helpful to you.

$$\int_0^\infty r^n e^{-\beta r} dr = \frac{n!}{\beta^{n+1}} \quad (1)$$

5a. Compute the mean distance of an electron from the nucleus of a one-electron atom with atomic number Z . (5 points)

$$\begin{aligned} r_{\text{mean}} &= \langle r \rangle = \langle \phi_{1s} | r | \phi_{1s} \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr} \right)^* r \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr} \right) r^2 \sin \theta d\phi d\theta dr \\ &= (4\pi) \left(\frac{Z^3}{\pi} \right) \int_0^\infty e^{-2Zr} r^3 dr \\ &= (4Z^3) \left(\frac{3!}{(2Z)^4} \right) = 4Z^3 \left(\frac{6}{16Z^4} \right) \\ &= \frac{3}{2Z} \text{ Bohr} \end{aligned}$$

5b. Compute the rms distance of an electron from the nucleus of a one-electron atom with atomic number Z . (5 points)

$$\begin{aligned} r_{\text{rms}} &= \sqrt{\langle r^2 \rangle} = \sqrt{\langle \phi_{1s} | r^2 | \phi_{1s} \rangle} = \sqrt{\int_0^\infty \int_0^\pi \int_0^{2\pi} \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr} \right)^* r^2 \left(\sqrt{\frac{Z^3}{\pi}} e^{-Zr} \right) r^2 \sin \theta d\phi d\theta dr} \\ &= \sqrt{(4\pi) \left(\frac{Z^3}{\pi} \right) \int_0^\infty e^{-2Zr} r^4 dr} \\ &= \sqrt{(4Z^3) \left(\frac{4!}{(2Z)^5} \right)} = \sqrt{4Z^3 \left(\frac{24}{32Z^5} \right)} = \sqrt{\frac{3}{Z^2}} \\ &= \frac{\sqrt{3}}{Z} \text{ Bohr} \end{aligned}$$

5c. Compute the most probable distance of an electron from the nucleus of a one-electron atom with atomic number Z . (5 points)

The probability of seeing an electron r units from the nucleus (at *any* angle) is

$$\begin{aligned} p(r) &= \int_0^\pi \int_0^{2\pi} |\phi_{1s}(r)|^2 r^2 \sin\theta d\phi d\theta \\ &= 4\pi r^2 |\phi_{1s}(r)|^2 = 4\pi \left(\frac{Z^3}{\pi} \right) r^2 e^{-2Zr} \\ &= 4Z^3 r^2 e^{-2Zr} \end{aligned}$$

The most probable distance is where this function has a maximum, which occurs where

$$\begin{aligned} 0 &= \frac{dp(r)}{dr} = 4Z^3 \left(\frac{d(r^2 e^{-2Zr})}{dr} \right) \\ 0 &= 4Z^3 (2r e^{-2Zr} - 2Zr^2 e^{-2Zr}) \\ 0 &= 2r - 2Zr^2 \\ 0 &= 1 - Zr \\ &\Downarrow \\ r_{mp} &= \frac{1}{Z} \end{aligned}$$

Bonus: (5 pts.) Derive the formula for the integral in Eq. (1).

Do this by induction. The $n=0$ case is obviously true, since the integral of a simple exponential gives

$$\int_0^\infty r^0 e^{-\beta r} dr = \int_0^\infty e^{-\beta r} dr = \left[\frac{-1}{\beta} e^{-\beta r} \right]_0^\infty = \left[0 - \frac{-1}{\beta} e^0 \right] = \frac{1}{\beta} = \frac{0!}{\beta^{0+1}}$$

Now suppose that the formula is true for some $n = k \geq 0$. I.e., assume that

$$\int_0^\infty r^k e^{-\beta r} dr = \frac{k!}{\beta^{k+1}}.$$

Differentiate both sides of the equation with respect to β , obtaining

$$\begin{aligned}
\int_0^\infty r^k e^{-\beta r} dr &= \frac{k!}{\beta^{k+1}} \\
\frac{\partial}{\partial \beta} \left(\int_0^\infty r^k e^{-\beta r} dr \right) &= \frac{\partial}{\partial \beta} \left(\frac{k!}{\beta^{k+1}} \right) \\
\int_0^\infty \frac{\partial(r^k e^{-\beta r})}{\partial \beta} dr &= k! \left(\frac{-(k+1)}{\beta^{k+2}} \right) \\
\int_0^\infty r^k (-r) e^{-\beta r} dr &= -\frac{(k+1) \cdot k!}{\beta^{k+2}} \\
-\int_0^\infty r^{k+1} e^{-\beta r} dr &= -\frac{(k+1)!}{\beta^{k+2}} \\
\int_0^\infty r^{k+1} e^{-\beta r} dr &= \frac{(k+1)!}{\beta^{k+2}}
\end{aligned}$$

Thus, if the equation is true for $n = k$, it is also true for $n = k + 1$. Since we know the equation is true for $n = k = 0$, we can, by induction, infer that it is true for $k = 1$, which implies that it is true for $k = 2$, which implies that it is true for $k = 3$, ...

Bonus: (5 pts.) Recall that the Heisenberg uncertainty principle states that, for particles in one dimension,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

For particles in three dimensions, one has the principle,

$$\sigma_r \sigma_p \geq \frac{3\hbar}{2} \quad (2)$$

which can be derived from the uncertainty in the individual components of the position/momentum. Verify, by computation of σ_r and σ_p , that Eq. (2) holds for the ground state of a one-electron atom.

We know that the average position of an electron in the hydrogen atom is the center of the atom which is $\mathbf{r} = 0$. So, using the result from 5b,

$$\begin{aligned}
\sigma_r^2 &= \langle \mathbf{r} \cdot \mathbf{r} \rangle - \langle \mathbf{r} \rangle^2 = \langle r^2 \rangle - \langle \mathbf{r} \rangle^2 = \frac{3}{Z^2} - 0 \\
\sigma_r &= \frac{\sqrt{3}}{Z}
\end{aligned}$$

Similarly, we know that the average momentum of the electrons is zero. So we have

$$\sigma_p^2 = \langle \mathbf{p} \cdot \mathbf{p} \rangle - \langle \mathbf{p} \rangle^2 = \langle p^2 \rangle - 0$$

The easiest way to evaluate the integral we need to do is to note that it is related to the kinetic energy, which in turn can be computed from the difference between the total energy and the potential energy. I.e.,

$$\langle p^2 \rangle = 2m \left\langle \frac{p^2}{2m} \right\rangle = 2mT = 2m(E - V)$$

For the electron in atomic units, $m = 1$. The energy is known, and the potential energy is given by an integral not unlike those we have already performed. So

$$\begin{aligned} \langle p^2 \rangle &= 2(E - V) = 2 \left(\frac{-Z^2}{2n^2} - \left\langle \phi_{1s} \left| \frac{-Z}{r} \right| \phi_{1s} \right\rangle \right) \\ &= 2 \left(\int_0^\infty \int_0^\pi \int_0^{2\pi} \left(\frac{Z^3}{\pi} \right) e^{-2Zr} \left(\frac{Z}{r} \right) r^2 \sin\theta \, d\phi \, d\theta \, dr - \frac{Z^2}{2(1)^2} \right) \\ &= 2 \left(4\pi \left(\frac{Z^3}{\pi} \right) (Z) \int_0^\infty r e^{-2Zr} \, dr - \frac{Z^2}{2(1)^2} \right) \\ &= 2 \left(4Z^4 \left(\frac{1!}{(2Z)^2} \right) - \frac{Z^2}{2(1)^2} \right) \\ &= 2 \left(Z^2 - \frac{Z^2}{2} \right) \\ &= Z^2 \end{aligned}$$

So now we have

$$\sigma_p = \sqrt{Z^2} = Z$$

Multiplying the two forms together, we have

$$\sigma_p \sigma_r = Z \left(\frac{\sqrt{3}}{Z} \right) = \sqrt{3} \geq \frac{3}{2} \hbar = \frac{3}{2}$$

where at the very end we have used the fact that $\hbar = 1$ in atomic units.