CH301H – Principles of Chemistry I: Honors
Fall 2011, Unique 51040

Exam 3
27 October 2011

Name: Key

You may use your textbook and a calculator for arithmetic.

Honor Code:

"The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community."

I certify that the work on this exam is entirely my own.

Signature Date

1. (20 points) True / False. Determine whether each of the following statements are true, false, or if there is no way to know (NWTK) with the given information.

a) True False NWTK — The Schrodinger equation can be solved exactly for any atom.

b) True False NWTK — In the Schrodinger equation, the variable E describes a constant which is equal to the energy of the wavefunction defined by ψ.

c) True False NWTK — $\psi = A\cos\theta$ is a wavefunction which solves the Schrodinger equation. Depends on A

d) True False NWTK — The radial part of the hydrogen atom wavefunction describes the shapes of the s, p, d, and f orbitals.

e) True False NWTK — The following is an allowed set of quantum numbers: $n = 3$, $l = 1$, $m = -1$, $m_s = +1$.

f) True False NWTK — For any value of the principle quantum number n, there are n^2 degenerate states. $2n^2$

g) True False NWTK — The energy of the hydrogen atom wavefunctions depend only on the radial portion of the wavefunction.

h) True False NWTK — The probability of finding an electron within a certain region of space can be known to arbitrarily high accuracy.

i) True False NWTK — A d orbital has 3 angular nodes.

j) True False NWTK — No two electrons are allowed to share a set of quantum numbers.

2. (8 points) Circle the multiple choice answer that correctly answers the question.

a) Which of the following describes the $1\sigma_u^*$ orbital in H_2^+?

i) this is an antibonding orbital
ii) this orbital has a node perpendicular to the internuclear axis
iii) this orbital is asymmetric with respect to inversion
iv) all of the above
v) none of the above

b) Which of the following describes the $2\pi_u$ orbital in H_2^+?

i) this is an antibonding orbital
ii) this orbital has a node perpendicular to the internuclear axis
iii) this orbital is asymmetric with respect to inversion
iv) all of the above
v) none of the above

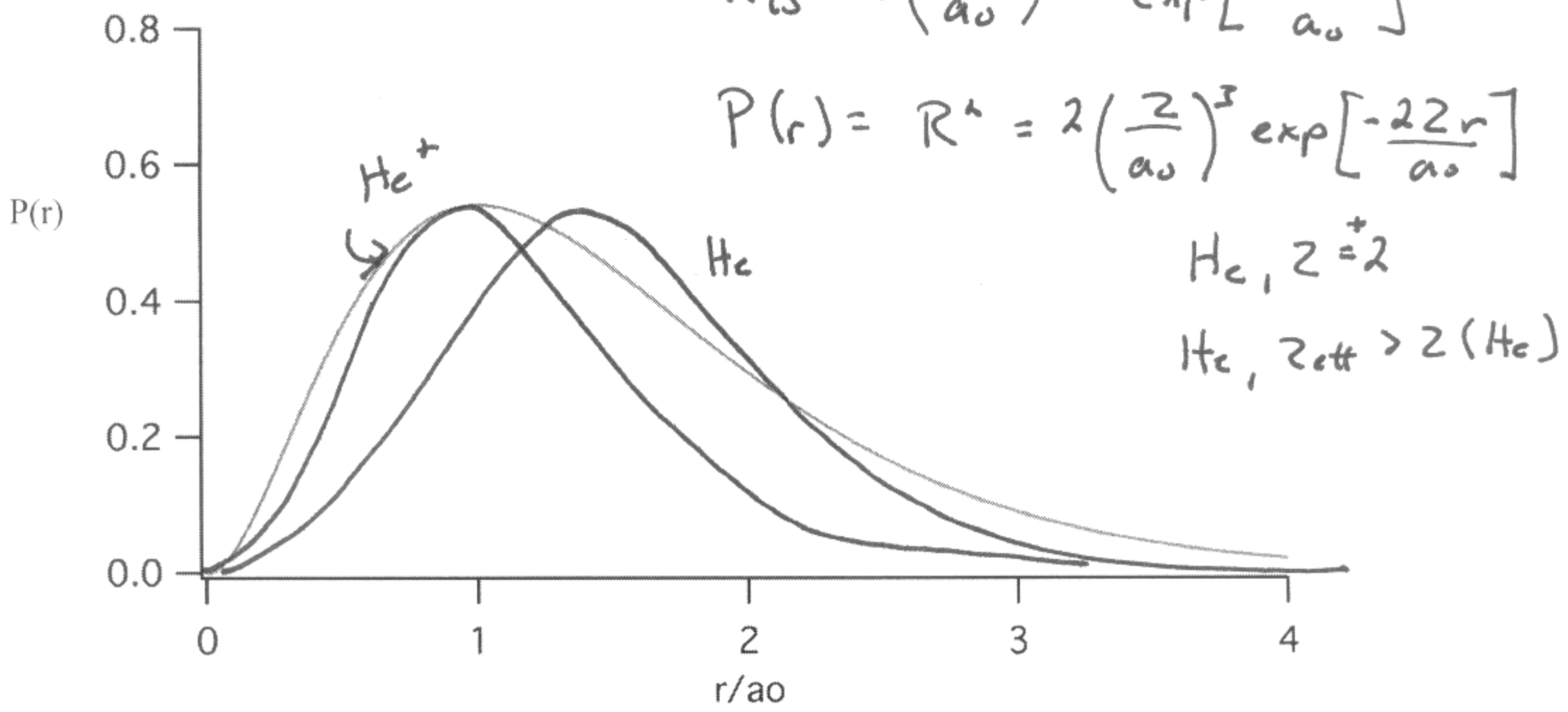
3. (12 points) Below is a plot of the radial probability density for 1s wave function in the hydrogen atom. On the same plot sketch what you think the radial probability density of the 1s function would look like for both He and He^+.

$$R_{1s} = 2\left(\frac{Z}{a_0}\right)^{3/2} \exp\left[-\frac{Zr}{a_0}\right]$$

$$P(r) = R^2 = 2\left(\frac{Z}{a_0}\right)^{3} \exp\left[-\frac{2Zr}{a_0}\right]$$

$He, Z = 2$

$He, Z_{eff} > 2 (He)$



4. (15 points) For each of the following valence electron configurations of a homonuclear diatomic molecule or molecular ion, identify the element X, Q, or Z, and determine the bond order.

a) X_2: $(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p)^4(\pi_g^* 2p)^4$

X = F

b) Q_2^-: $(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p_z)^1$

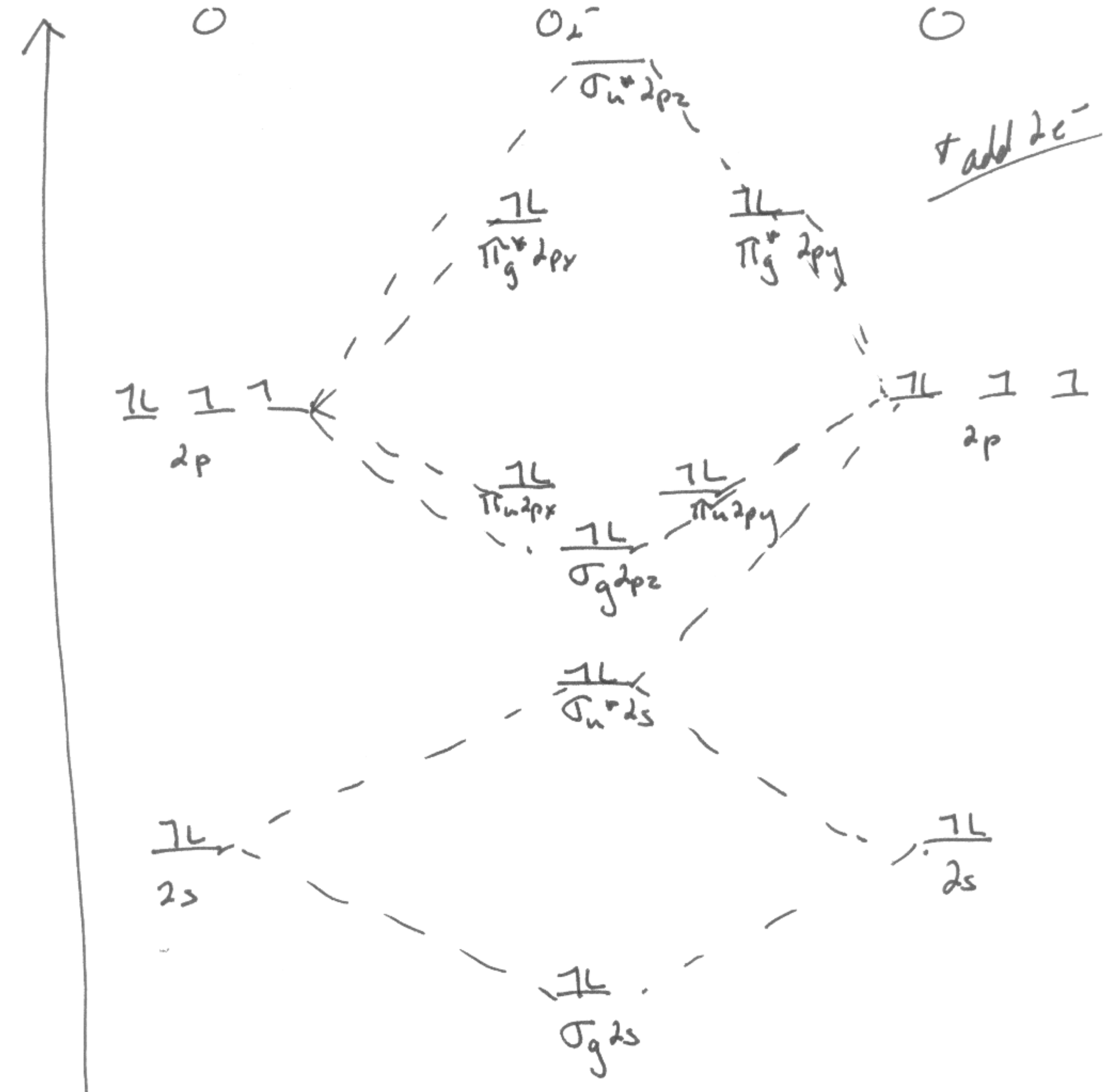
Q = C

c) Z_2^{2+}: $(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p)^4(\pi_g^* 2p)^2$

Z = F

5. (35 points) When one electron is added to an oxygen molecule, a superoxide ion is formed. The addition of two electrons gives a peroxide ion. Removing an electron gives a positively charged molecular oxygen cation.

a) Construct a molecular orbital diagram of the peroxide ion.



b) For each of the four species mentioned above, give the valence electron configuration of the molecule and the bond order.

O_2 : $(\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\sigma_g 2p^2)^2 (\pi_u 2p_x)^2 (\pi_u 2p_y)^2 (\pi_g^* 2p_x)^1 (\pi_g^* 2p_y)^1$

O_2^- : $(\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\sigma_g 2p_z)^2 (\pi_u 2p_x)^2 (\pi_u 2p_y)^2 (\pi_g^* 2p_x)^2 (\pi_g^* 2p_y)^1$

O_2^{2-} : $(\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\sigma_g 2p_z)^2 (\pi_u 2p_x)^2 (\pi_u 2p_y)^2 (\pi_g^* 2p_x)^2 (\pi_g^* 2p_y)^2$

O_2^+ : $(\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\sigma_g 2p_z)^2 (\pi_u 2p_x)^2 (\pi_u 2p_y)^2 (\pi_g^* 2p_x)^1$

(ok to abbreviate this in some rational and clear way)

c) Determine which of the four species mentioned above are paramagnetic.

anything w/ an unpaired e^- : O_2, O_2^-, O_2^+ are all paramagnetic

d) Rank these four species in order of increasing bond dissociation energy.

O_2 : $BO = \frac{6-2}{2} = 2$

O_2^- : $BO = \frac{6-3}{2} = \frac{3}{2}$

O_2^{2-} : $BO = \frac{6-4}{2} = 1$

O_2^+ : $BO = \frac{6-1}{2} = \frac{5}{2}$

$O_2^{2-} < O_2^- < O_2 < O_2^+$

$\longrightarrow$ increasing bond dissociation energy

e) The superoxide ion is extremely reactive and very harmful when exposed to biological tissues. Using any information from parts a) – d), offer a plausible reason why superoxide would be so reactive.

The one unpaired e^- in O_2^- would rather be given up or accept another e^- from another source. This will make it very reactive w/ any other molecule it encounters.

6. (10 points) The ionization energy of molecular hydrogen is greater than that of atomic hydrogen, but the ionization energy of molecular oxygen is lower than that of atomic oxygen. Using some combination of words, figures, or equations, explain this observation.

The electron configuration of O_2 shows that the e^- that will be ionized is coming from a high energy π_g^* orbital that is higher in energy than the 2p AO of oxygen. This means it will be easier to remove this e^- in O_2 than in O. The opposite is true in H_2; the e^- from H_2 is coming from a σ_g orbital that is lower in energy than the H atom 1s orbital, and thus more difficult to remove.