

## Practice Exam 1 – Solution

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Useful Formulas:

- **Magnetization**  $M$  of a multiplet with a given total angular momentum  $J$  and Landé  $g$ -factor  $g_J$  is given by

$$M = Ng_J\mu_B J B_J(x), \text{ where}$$

$$x = \frac{g_J\mu_B JB}{k_B T} \text{ and}$$

$$\mu_B = \frac{e\hbar}{2m} = 5.8 \times 10^{-5} \text{ eV/T} \text{ is the Bohr magneton.}$$

The Brillouin function is given by

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right).$$

It may be approximated by

$$B_J(x) \approx \frac{J+1}{3J} x \text{ for } x \ll 1.$$

- **Hydrogen atom ( $Z=1$ ):**

$$R = \frac{me^4}{2\hbar^2} = 13.6 \text{ eV} \text{ Rydberg constant}$$

$$a_B = \frac{\hbar^2}{me^2} = 0.529 \text{ \AA} \text{ Bohr radius}$$

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1. (5 points) X-ray laser pulses can be used to strip atoms of electrons one by one (ionize the atom).

(a) What is the energy required to remove the last electron from a K atom? The neutral K atom has 19 electrons. The ionization energy of the hydrogen atom is 13.6 eV.

(b) What is the size of the Bohr radius for this last electron?

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*Solution:*

(a) The last electron sees  $Z = 19$ . The ionization energy  $E_I$  is proportional to  $Z^2$ .  $E_I$  for the hydrogenic atom with  $Z = 19$  is  $E_I = 13.6 \text{ eV} \times 19^2 = 4909.6 \text{ eV}$ .

(b) The Bohr radius  $a_B$  shrinks and scales as  $1/Z$ . The new Bohr radius is  $a_B = 0.529 \text{ \AA} / 19 = 0.0274 \text{ \AA}$ .

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2. (5 points) Consider an electron trapped in a 3-dimensional harmonic oscillator potential. The Hamiltonian in atomic units ( $\hbar = m = e^2 = 1$ ) is given by

$$H = -\frac{1}{2}\nabla^2 + \frac{1}{2}r^2.$$

Let's use a trial wave function for the ground state of the form

$$\psi(\vec{r}) = \frac{1}{\sqrt{\pi\alpha^3}} e^{-r/\alpha}.$$

This gives (do **not** derive this)

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{1}{2\alpha^2} + \frac{3}{2}\alpha^2.$$

What is the best variational ground state energy one can get (in Hartree units)?

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*Solution:*

$$E(\alpha) = \frac{1}{2\alpha^2} + \frac{3}{2}\alpha^2.$$

Minimize  $E(\alpha)$  with respect to the variational parameter  $\alpha$ :

$$\frac{dE(\alpha)}{d\alpha} = -\frac{2}{2}\alpha^{-3} + \frac{3}{2}2\alpha = 0.$$

This gives the best variational parameter  $\alpha^2 = 1/\sqrt{3}$  (make sure this is a minimum, not a maximum).

Substituting this value of  $\alpha^2$  in the energy expression we find

$$E_{min} = E(\alpha^2 = 1/\sqrt{3}) = \sqrt{3} \text{ Hartree}.$$

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3. (10 points) The ground state electronic configuration of the nitrogen atom is  $1s^2 2s^2 2p^3$ . Treat the  $1s$  and  $2s$  electrons as core electrons and the  $2p$  electrons as valence electrons.

(a) What is the total spin angular momentum and total orbital angular momentum of the core? Do these core electrons contribute to the magnetic susceptibility  $\chi$  of the atoms? If so, what is the sign of  $\chi$ ?

- (b) According to Hund's rules, what is the lowest energy multiplet and what is its degeneracy?
- (c) What is the expression for zero-field magnetic susceptibility of 1 mole of nitrogen atoms at high temperatures  $T$ ?

*Solution:*

- (a)  $S = 0, L = 0, J = 0$ : No paramagnetism. There is a negative (usually) small diamagnetic contribution to the magnetic susceptibility (Langevin diamagnetism).
- (b)  $S = 3/2, L = 0, J = 3/2$ :  $^4S_{3/2}$   
 Degeneracy of this lowest energy multiplet is  $2J + 1 = 4$ .
- (c)  $x = \frac{g_J \mu_B J B}{k_B T} \ll 1$  at high temperatures, leading to Curie law

$$\chi = \frac{M}{B} = N_A \frac{(g_J \mu_B)^2 J(J+1)}{3k_B T} .$$

We have  $S = 3/2, L = 0, J = 3/2$ , thus

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} = 1 + 1 = 2 .$$

Then,

$$\chi = N_A \frac{5\mu_B^2}{k_B T} .$$

4. (5 points) A He atom is excited to the  $1s^1 2p^1$  configuration. The one-electron spatial wave functions are  $\phi_{1s}(\vec{r})$  and  $\phi_{2p_m}(\vec{r})$ .

- (a) What is the total number of 2-electron states corresponding to this configuration?
- (b) Write down the 2-electron spin triplet excited state wave functions associated with this configuration.

*Solution:*

- (a) Since 1 electron has to be in the  $1s$  state with spin either up or down (2 possible ways) and the other in one of the 6  $2p$  states (three space orbitals with spin either up or down – 6 possible ways), the total number of 2-electron states is  $2 \times 6 = 12$ .
- (b) There are 9 possible triplet excited wavefunctions,

$$\begin{aligned} \psi_{t_1} &= \frac{1}{\sqrt{2}} [\phi_{1s}(\vec{r}_1) \phi_{2p_m}(\vec{r}_2) - \phi_{1s}(\vec{r}_2) \phi_{2p_m}(\vec{r}_1)] \times [\alpha_1 \alpha_2] , \\ \psi_{t_2} &= \frac{1}{\sqrt{2}} [\phi_{1s}(\vec{r}_1) \phi_{2p_m}(\vec{r}_2) - \phi_{1s}(\vec{r}_2) \phi_{2p_m}(\vec{r}_1)] \times [\beta_1 \beta_2] , \\ \psi_{t_3} &= \frac{1}{\sqrt{2}} [\phi_{1s}(\vec{r}_1) \phi_{2p_m}(\vec{r}_2) - \phi_{1s}(\vec{r}_2) \phi_{2p_m}(\vec{r}_1)] \times \left[ \frac{\alpha_1 \beta_2 + \beta_1 \alpha_2}{\sqrt{2}} \right] , \end{aligned}$$

each with  $m = -1, 0, 1$ .

5. (5 points)

- (a) Write down the wave function for the ground state of the  $H_2$  molecule in the molecular orbital (MO) approximation. Express your answer in terms of the  $1s$  hydrogen atom wave functions associated with the two protons,  $a(\vec{r})$  and  $b(\vec{r})$ .
- (b) Draw qualitatively the ground state electronic energy, the repulsive energy between two protons, and the total energy as function of the inter-nuclear separation  $R$ .

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*Solution:*

- (a) In the MO approximation for the  $H_2$  molecule we first find **single particle** states (molecular orbitals). In the simplest case the molecular orbital is formed out of two atomic hydrogen  $1s$  states associated with two nuclei, denoted as  $a(\vec{r})$  and  $b(\vec{r})$ . Since the bonding combination has lower energy we use these bonding orbitals to construct the states for the **two** electrons.

$$\phi_B(\vec{r}) = N[a(\vec{r}) + b(\vec{r})].$$

If we now put two electrons in this orbital, their spins are opposite. We get the **spin singlet**

$$\psi_{MO}(\vec{r}_1, \vec{r}_2) = \phi_B(\vec{r}_1)\phi_B(\vec{r}_2) \left[ \frac{\alpha_1\beta_2 - \alpha_2\beta_1}{\sqrt{2}} \right].$$

This is just like the ground state of the He atom. Instead of putting the two electrons in the  $1s$  orbital  $\phi_{1s}(\vec{r})$ , we put them into the bonding orbital  $\phi_B(\vec{r})$ .

- (b)

