Practice Exam 1 – Solution

Student Name:

Useful Formulas:

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

$$
\begin{aligned}
M &= N g_J \mu_B J B_J(x) \text{ , where} \\
x &= \frac{g_J \mu_B J B}{k_B T} \text{ and} \\
\mu_B &= \frac{e\hbar}{2m} = 5.8 \times 10^{-5} \text{ eV/T} \quad \text{is the Bohr magneton.}
\end{aligned}
$$

  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

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

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

$$
\begin{aligned}
R &= \frac{me^4}{2\hbar^2} = 13.6 \text{ eV} \quad \text{Rydberg constant} \\
a_B &= \frac{\hbar^2}{me^2} = 0.529 \text{ Å} \quad \text{Bohr radius}
\end{aligned}
$$

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?

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 $E_I = 13.6$ eV $\times 19^2 = 4909.6$ eV.

(b) The Bohr radius a_B shrinks and scales as $1/Z$. The new Bohr radius is $a_B = 0.529$ Å$/19 = 0.0274$ Å.

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)

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

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

Solution:

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

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

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

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

Substituting this value of α^2 in the energy expression we find

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

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 χ of the atoms? If so, what is the sign of χ?

(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

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

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,

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

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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 $m = -1, 0, 1$.

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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.

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.

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

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

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

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 $\phi_g(\vec{r})$.

(b)

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