

KEY

3rd Exam (90 pts. possible)Please budget your time carefully and show all work for partial credit. Read each problem carefully!

$h = 6.62607 \times 10^{-34} \text{ J s}$	$1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$	$\int_0^{\infty} r^n e^{-ar} dr = \frac{n!}{a^{n+1}}$
$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$	$1 \text{ amu} = 1.66054 \times 10^{-27} \text{ kg}$	
$c = 2.997925 \times 10^8 \text{ m/s}$	$E_{H\text{-like}} = -\frac{Z^2}{2n^2} \text{ hartrees}$	

(1) (15 pts.) Consider a hydrogen atom in a $2p$ excited state with a wavefunction given by (in atomicunits): $\psi_{2p_0} = R_{2,1}(r)Y_{1,0}(\theta, \phi)$, where $R_{2,1} = \frac{1}{\sqrt{24}} r e^{-r/2}$ and $Y_{1,0} = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta$. Determine theaverage value of r in this state regardless of the angles, where r is the radial distance of the electron from the proton.

$$\begin{aligned} \langle r \rangle &= \int_0^{\infty} |R_{2,1}|^2 r^2 dr = \frac{1}{24} \int_0^{\infty} r^5 e^{-r} dr \\ &= \frac{1}{24} \left[\frac{5!}{1^6} \right] = 5.0 \text{ bohr} \end{aligned}$$

(2) (40 pts) Consider the Be atom.

(a) Write the full hamiltonian operator for this atom using SI or atomic units.

$$\hat{H} = \frac{-\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \nabla_4^2) - \frac{4e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} + \frac{1}{r_4} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \frac{1}{r_{34}} \right)$$

(b) Consider its $1s^2 2s^1 2p^1$ excited state configuration. What is the energy of this state in the independent particle approximation? (use atomic units)

$$E_n = \frac{-Z^2}{2n^2} = \frac{-16}{2n^2}$$

$$E_{\text{IPA}} = 2E_{1s} + E_{2s} + E_{2p} = 2 \left(\frac{-16}{2} \right) + \left(\frac{-16}{2 \cdot 4} \right) + \left(\frac{-16}{2 \cdot 4} \right) = -16 - 2 - 2 = -20 E_h$$

(c) Now determine the possible terms and levels of the configuration of part (b), i.e., find the term symbols. How many states are associated with each term?

$$\begin{array}{l} l_1=0 \\ l_2=1 \end{array} \left. \vphantom{\begin{array}{l} l_1=0 \\ l_2=1 \end{array}} \right\} L=1$$

$$\begin{array}{l} s_1=1/2 \\ s_2=1/2 \end{array} \left. \vphantom{\begin{array}{l} s_1=1/2 \\ s_2=1/2 \end{array}} \right\} S=0, 1$$

$$\begin{array}{l} {}^1P_1, {}^3P_2, {}^3P_1, {}^3P_0 \\ \uparrow \\ 3 \text{ states} \end{array} \quad \underbrace{{}^3P_2, {}^3P_1, {}^3P_0}_{5+3+1 = 9 \text{ states}}$$

- (d) From your results of part (c), chose the level with the largest value of J and write a Slater determinant wavefunction for the state with $M_J = +J$. Be as specific as possible in labeling the spin-orbitals chosen for your determinant. (Hint: remember that $M_J = M_L + M_S$ and use this to determine which p_{m_l} orbital is occupied)

$${}^3P_2 \quad \text{for } m_J = 2 \quad : \quad \frac{1}{2s} \quad \frac{1}{-1} \quad \frac{1}{0} \quad \frac{1}{1} \quad 2p \quad \begin{matrix} m_L = 1 \\ m_S = 1 \\ m_J = 2 \end{matrix}$$

spin-orbitals: $1s\alpha, 1s\beta, 2s\alpha, 2p_1\alpha$

$$\Psi = \frac{1}{\sqrt{4!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & 2p_1(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & 2p_1(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) & 2p_1(3)\alpha(3) \\ 1s(4)\alpha(4) & 1s(4)\beta(4) & 2s(4)\alpha(4) & 2p_1(4)\alpha(4) \end{vmatrix}$$

- (3) (15 pts.) Consider the three real p -type functions used in descriptions of chemical bonding:

$$p_x = \frac{1}{\sqrt{2}}(Y_{1,-1} - Y_{1,1}), \quad p_y = \frac{i}{\sqrt{2}}(Y_{1,-1} + Y_{1,1}), \quad \text{and } p_z = Y_{1,0},$$

where $Y_{l,m}$ are the usual spherical harmonic functions.

- (a) Determine which of these are eigenfunctions of ℓ^2 or ℓ_z (if any). Give the eigenvalues where possible (do not use atomic units). Show all work.

$$\ell^2 p_x = \frac{1}{\sqrt{2}} [\ell^2 Y_{1,-1} - \ell^2 Y_{1,1}] = 2\hbar^2 p_x \quad \checkmark$$

$$\ell^2 p_y = \frac{i}{\sqrt{2}} [\ell^2 Y_{1,-1} + \ell^2 Y_{1,1}] = 2\hbar^2 p_y \quad \checkmark$$

$$\ell^2 p_z = \ell^2 Y_{1,0} = 2\hbar^2 p_z \quad \checkmark$$

$$\ell_z p_x = \frac{1}{\sqrt{2}} [\ell_z Y_{1,-1} - \ell_z Y_{1,1}] = \frac{1}{\sqrt{2}} [-\hbar Y_{1,-1} - \hbar Y_{1,1}] \neq c p_x$$

$$\ell_z p_y = \frac{i}{\sqrt{2}} [\ell_z Y_{1,-1} + \ell_z Y_{1,1}] = \frac{i}{\sqrt{2}} [-\hbar Y_{1,-1} + \hbar Y_{1,1}] \neq c p_y$$

$$\ell_z p_z = \ell_z Y_{1,0} = 0 \hbar Y_{1,0} \quad \checkmark \quad \text{eigenvalue of zero.}$$

(b) Briefly state or describe the theorem that was used to construct/justify these p_x and p_y functions.

Linear combinations of degenerate eigenfunctions are still eigenfunctions of the same operator. ℓ^2 in this case.

(4) (20 pts.) A normalized trial function of the form (in atomic units) $\phi = \left[\frac{(2\beta)^7}{4\pi 6!} \right]^{1/2} r^2 e^{-\beta r}$, where β is an adjustable parameter, is used in the variation method to obtain the lowest possible energy for the hydrogen atom ground state. An intermediate result along this process is $\int \phi H \phi d\tau = \frac{\beta^2}{10} - \frac{\beta}{3}$.

(a) Complete the variational calculation to obtain the optimal β and the best value of the trial energy.

$$E_{\text{trial}} = \frac{\beta^2}{10} - \frac{\beta}{3} \quad \text{for minimum: } \frac{\partial E_{\text{trial}}}{\partial \beta} = 0$$

$$= \frac{2\beta}{10} - \frac{1}{3}$$

$$\text{so } \beta_{\text{opt}} = \frac{10}{6}$$

$$E_{\text{trial}} = \frac{(10/6)^2}{10} - \frac{(10/6)}{3} = -\frac{10}{36} = -\frac{5}{18} E_h$$

(b) What is the percent error in this result? Qualitatively, can you explain why this trial function maybe doesn't perform so well?

$$\text{exact: } E_{n=1} = -\frac{1}{2} E_h$$

$$\% \text{ error} = \frac{-5/18 - (-1/2)}{-1/2} \times 100 = 44.4\%$$

our trial function goes to zero as $r \rightarrow 0$, whereas the exact wavefunction stays finite and has a cusp.
non-zero