

**Quantum Mechanics and Spectroscopy**  
**CHEM 3PA3**  
**Assignment 17**

Name: \_\_\_\_\_

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1. Considering the Born-Oppenheimer approximation and neglecting the electron-electron interactions, what would be the energy of a 5 electron atom?

2. A Helium cation ( $\text{He}^+$ ) is described by the following wavefunction,

$$\Psi_{\text{He}^+}(\mathbf{r}, t) = 0.5774\psi_{3s}(\mathbf{r}, t) - 0.7071\psi_{3p_1}(\mathbf{r}, t) + 0.4082\psi_{3d_2}(\mathbf{r}, t).$$

Here,  $\psi_{\text{label}}$  are the normalized eigenfunctions of the  $\text{He}^+$  Hamiltonian and the subscripts indicate the  $n$ ,  $l$  and  $m_l$  quantum numbers.

- (a) What is the expectation value for the energy in this system in atomic units?
  - (b) What is the expectation value of the square magnitude of the total orbital angular momentum in terms of  $\hbar$ ?
  - (c) What is the expectation value for the amount of orbital angular momentum about the  $z$  axis in terms of  $\hbar$ ?
  - (d) What is the probability of obtaining "zero" when measuring the total orbital angular momentum of this system?
  - (e) Does  $\Psi(\mathbf{r}, t)$  describe a stationary state?
3. Use first-order perturbation theory to calculate the first-order correction to the ground-state energy of a quartic oscillator whose potential energy is  $V(x) = cx^4$ . In this case, use a harmonic oscillator as the unperturbed system. What is the perturbing potential?
4. Consider a system subject to the potential  $V(x) = kx^2/2 + \gamma_3x^3/6 + \gamma_4x^4/24$ . Calculate the ground-state energy of this system using a trial function of the form  $\phi = c_1\psi_0(x) + c_2\psi_2(x)$ , where  $\psi_n$  are the harmonic-oscillator wavefunctions.
5. What are the values for the following quantum numbers for a state described by  $^5I$  term symbol? When the term symbol is not sufficient to fully specify the quantum number, please list all the possible values.
- (a)  $L$  (total orbital angular momentum)
  - (b)  $M_L$  (orbital angular momentum around the  $z$ -axis)
  - (c)  $S$  (total spin angular momentum)
  - (d)  $M_S$  (spin angular momentum around the  $z$ -axis)
6. What are the term symbols associated with the electron configurations,  $2p^13p^1$  and  $2p^2$ ?
7. An excited state of atomic calcium has the electron configuration  $1s^22s^22p^63s^23p^63d^14f^1$ ,
- (a) Derive all the term symbols for this electron configuration.
  - (b) Which term symbol corresponds to the lowest energy of this configuration?