Chem 4531, Problem Set #8, Fall 2016

To be returned before class on Friday, November 4

1. Using first order, non-degenerate perturbation theory, evaluate the perturbed ground state energy of an anharmonic oscillator with the Hamiltonian

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 + cx^3 + dx^4 \]  

(4 points)

2. Obtain the optimum value of the parameter c and estimate the ground-state energy of the one-dimensional harmonic oscillator using \( \phi(x) = e^{-cx^2} \) as a trial function, and verify that the solutions are identical to exact solutions of the Schrödinger equation (4 points)

3. The energy of an electronic level is observed to increase by 1.39 meV when a 12 Tesla magnetic field is applied. What is the magnetic quantum number of this electron? (4 points)

4. The spin-orbit wavefunction of a multi-electron state (i.e. describing the spatial orbital and the electron spin) must take into account both that electrons are indistinguishable, and that the total wavefunction must be anti-symmetric with respect to exchange of two electrons. Considering as an example the first excited state of He, with electron configuration 1s\(^1\) 2s\(^1\), this state can be drawn with arrow diagrams:

\[
\begin{array}{cccc}
2s & & & \\
\uparrow & \downarrow & \downarrow & \downarrow \\
1s & & & \\
\uparrow & \uparrow & \downarrow & \downarrow \\
\end{array}
\]

or written as linear combination of spin-orbit terms, (e.g. \( \psi_{1s}^{1}(1) \psi_{1s}^{2}(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \) as you saw in class for two electrons in one orbital) or written as the appropriately normalized determinant of a matrix, which is called a Slater determinant (see, e.g. equation 10.78 in S.A.B). Write the determinantal wavefunctions that correspond to each of the four states in the arrow diagram for the 1s\(^1\) 2s\(^1\) configuration. It may be helpful to review S.A.B. section 10.8 (4 points)

5. Write down the ground state electron configuration of Al and all possible term symbols describing this configuration. (4 points)
6. Write all possible terms describing the electron configuration of Sc: \(1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^1 \ 4s^2\) (4 points)

7. Consider the He atom with its two electrons. Write all the possible excited-state terms associated with one electron in the K shell and the other in the L shell. (4 points)

8. In a spectroscopy experiment, it’s important to know which transitions are allowed or forbidden, to assess if the measured spectra are consistent with expectations. For the following transitions, which are allowed, which are forbidden, and if the latter, why? (7 points)

a. \(\text{H} (1s^2S_{1/2}) \rightarrow \text{H} (2p^2P_{1/2})\)

b. \(\text{H} (1s^2S_{1/2}) \rightarrow \text{H} (3d^2D_{3/2})\)

c. \(\text{H} (1s^2S_{1/2}) \rightarrow \text{H} (3p^2P_{3/2})\)

d. \(\text{He} (1s^1S_0) \rightarrow \text{He} (2p^3P_1)\)

e. \(\text{Ar} (3p^1S_0) \rightarrow \text{Ar} (4s^1P_0)\)

f. \(\text{Ar} (3p^1S_0) \rightarrow \text{Ar} (4p^1P_0)\)

g. \(\text{Na} (3s^2S_{1/2}) \rightarrow \text{Na} (3p^2P_{1/2})\)