

Practice Questions for CHEM 4010, set #2

In addition to the questions below, it is a good practice for you to try to answer the Multiple Choice Questions at the end of each chapter in Lowe and Peterson's "Quantum Chemistry".

1) Spherical harmonics $Y_{l,m}(\theta, \phi)$ are eigenfunctions of the z -component angular momentum operator \hat{L}_z , $\hat{L}_z Y_{l,m}(\theta, \phi) = Y_{l,m}(\theta, \phi) \times \text{constant}$. In that equation, what is the "constant", ie, the eigenvalue?

2) What is the magnitude of the angular momentum for a d -type atomic orbital?

3) What happens to the $n = 3$ energy levels of a H atom when it is placed in a magnetic field? Make a diagram to show the energy levels before and after applying the magnetic field.

4) What is the reduced mass in kg for the CO molecule? Use $m(^{12}C) = 12$ a.m.u. exactly, $m(^{16}O) = 15.9949$ a.m.u., and $1 \text{ a.m.u.} = 1.660540 \times 10^{-27}$ kg.

5) The energy levels of a rigid rotor are given by $E = J(J + 1)\hbar^2/2I$, and the moment of inertia of a diatomic molecule is given by $I = \mu r^2 = (M_A M_B / (M_A + M_B))r^2$. With a combination of words and equations, explain how you could calculate the bond length of a diatomic molecule AB if you had the frequency of absorption corresponding to the $J = 3$ to $J = 4$ transition in a microwave spectrum, $\nu_{3,4}$, and you knew the precise masses of the two atoms M_A and M_B .

6) Use atomic units and write the hamiltonian for two electrons moving in the field of a fixed nucleus of charge $+2$. Make sure you define each symbol in the expression for the hamiltonian.

7) An approximate (trial) wavefunction for the two electrons of a He atom in a $1s2s$ configuration is $\Psi(\vec{r}_1, \vec{r}_2) = \sqrt{8/\pi} e^{-2r_1} \sqrt{1/\pi} (1 - r_2) e^{-r_2}$
There is a fundamental flaw with that wavefunction: what is it?

8) In trying to obtain an approximate wavefunction for the two electrons of a He atom, one normally makes the *independent electron approximation*. What is the independent electron approximation?

9) State the *exclusion principle* as best as you can.

10) In general terms, what is a Slater determinant and why is it so useful in electronic structure theory? As an example, give the Slater determinant corresponding to the $1s(\uparrow)2s(\uparrow)$ configuration of He.

11) Make a qualitatively correct energy level diagram that shows the 5 states corresponding to the $1s^2$ and $1s2s$ electron configurations of the He atom.

12) A normalized function f is defined as follows:

$$f = 0.3714 \psi_{1s} + 0.5571 \psi_{2p_1} + 0.7428 \psi_{3d_2}$$

where ψ_{1s} is the normalized eigenfunction for the $1s$ state of the hydrogen atom, ψ_{2p_1} is the normalized $2p_1$ eigenfunction, and ψ_{3d_2} is the normalized $3d_2$ eigenfunction. Evaluate the average value of the z component of angular momentum in a.u., and the average energy also in a.u., for this function.

13) What hydrogen atomic orbital is this? Give the 3 quantum numbers n , ℓ and m_ℓ .

$$-\frac{1}{\sqrt{8\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} \exp(-r/2a_0) \sin\theta \exp(i\phi)$$

14) What are the SI units attached to the angular momentum \vec{L} ?

15) We seek to write a qualitatively correct wavefunction for the $1s^1 2s^1$ configuration of the He atom. If the spatial part of the wavefunction is $\frac{1}{\sqrt{2}}(1s(1)2s(2) + 2s(1)1s(2))$, what is the spin part of the wavefunction?

16) An approximate expression for the energy of the triplet of states of the He atom in the $1s^1 2s^1$ configuration is $E_3 \approx E_{1s} + E_{2s} + J - K$. In that expression, what do the symbols J and K represent?

17) The iron atom in its ground state has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. Estimate as best as you can the effective nuclear charge appropriate for the 3s atomic orbital of the iron atom in its ground state. Explain your reasoning.

18) Consider the Be atom in the excited state configuration $1s^2 2s^1 2p^1$.

(a) How many states are there with that configuration?

(b) One of the terms for this configuration is 1P_1 . Give the values of L , S and J for this term, and give its degeneracy.

19) Suppose we have a collection of H atoms, each of which is in a state described by the normalized wavefunction ϕ , $\phi = 0.900\psi_{1s} + 0.436\psi_{2s}$, where ψ_{1s} and ψ_{2s} are the familiar 1s and 2s atomic orbitals. We measure the energy for each of these H atoms.

(a) What are the possible values, in atomic units, for each measurement of the energy?

(b) What is the average energy, in atomic units, measured for all those H atoms?

20) What is the variational principle?

21) For a free particle moving along a line (along x), the hamiltonian is $\hat{H} = (-\hbar^2/2m)\frac{d^2}{dx^2}$ and the momentum operator is $\hat{p} = -i\hbar\frac{d}{dx}$. Is it possible to measure the energy and the momentum of a free particle simultaneously and with perfect precision? Explain.

22) A general formula for the uncertainty relation for the simultaneous measurement of properties A and B is: $\sigma_A\sigma_B \geq \frac{1}{2} | \langle [\hat{A}, \hat{B}] \rangle |$

(a) What does σ_A represent? (You can use words or equations to answer)

(b) Suppose the wavefunction is ψ ; use words and equations to explain how you would evaluate the right-hand side of the inequality.