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● PROBLEMS

1. A magnetic dipole with strength 1.2 Bohr magnetons is in a uniform magnetic field whose strength is 500 oersted. What is the difference in energy between the orientations of the dipole parallel (north–to–north) and antiparallel (north–to–south) to the applied magnetic field? Suppose the dipole has the low-energy orientation; the application of an oscillatory magnetic field at the appropriate frequency can induce absorption of energy and the eventual transition to the high-energy orientation. Sketch the system, indicating the dipole, the external field and the oscillatory field, at three specified times during a single cycle. Be careful to show the *directions* of all vectors. What is the resonant frequency of the dipole in the given field?

2. Using a classical expression analogous to Eq. 5.4, compute the magnetic moment of a 500-g sphere of metal on a 1-m string, whirling at a rate of 1 revolution per second, and carrying an excess negative charge of 10^{-12} $\mathscr{F}$. (One faraday, $\mathscr{F}$, is 1 mol of electrons, or 96,485 C.) What is the energy of interaction of this magnetic dipole with the earth's magnetic dipole if the two are parallel?

3. Compute the frequency of the electromagnetic radiation associated with a transition of an electron between the state with $m_s = +\frac{1}{2}$ and the state with $m_s = -\frac{1}{2}$, if the electron is in a field of 0.5 T (5000 gauss). Compute the corresponding frequency if the particle is a proton instead of an electron.

4. A Stern–Gerlach experiment is conducted with silver atoms passing through a magnetic field whose gradient is 3×10^2 T/m. The length of the region of the field gradient is 0.05 m. The particles travel 0.5 m to their target surface after leaving the field with initial speed 10^5 m/s. How far apart are the points where the two emerging

beams strike the target? (Recall the analysis of Thomson's experiment to determine e/m.)

5. Sodium atoms are put through a Stern–Gerlach apparatus and separated into two beams of equal intensity as shown in Fig. 5A.2a. The beam corresponding to $M_S = +\frac{1}{2}$ is then put through a second pair of magnets whose orientation is rotated about the beam axis through an angle θ with respect to the first pair of magnets. Figures 5A.2b and 5A.2c correspond to special cases with $\theta = 180°$ and $\theta = 90°$, respectively. Calculate the relative intensities of the beams with $M_S' = +\frac{1}{2}$ and $M_S' = -\frac{1}{2}$ for arbitrary θ. Ignore the small nonzero angle at which the beam emerges from the first separating device.

6. Explain, in terms of the symmetry of the forces exerted on an electron, why l and m are good quantum numbers for each electron in the central field model, but not in real atoms.

7. The most probable value of each electron–nuclear distance in H⁻ is 1.178 bohr; the average value of the electron–nuclear distance is 2.707 bohr. What qualitative inferences can one make about the shape of the electron probability density from a comparison of these two numbers?

8. Within a series of isoelectronic ions such as Li, Be⁺, B²⁺, C³⁺, and so on, the relative contribution of the correlation energy to the total energy of the system diminishes with increasing nuclear charge. Explain.

9. Prove that $\frac{27}{16}$ is the value of the "effective nuclear charge" Z' of Eq. 5.13 that minimizes the expectation value E' of energy (Eq. 5.11) when $\psi^{(2)}(r_1, r_2)$ of Eq. 5.13 is used to evaluate E'.

10. Put the entries in the following sets of configurations in order of increasing energy. Then check your intuition by comparing the results with the experimental results from atomic spectroscopy, as given, for example, by C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards Circular 467).
    (a) Li, $1s^2 2s$
    $1s 2s^2$
    $1s 2s 2p$
    $1s^2 2p$
    (b) C, $1s^2 2s^2 2p^2$
    $1s^2 2s 2p^3$
    $1s 2s^2 2p^3$
    $1s^2 2s^2 2p 3s$

11. Using the tables given by C. E. Moore in *Atomic Energy Levels* (National Bureau of Standards Circular 467),

compute the energies of the following atomic configurations by taking the appropriately weighted averages of the atomic state energies in the tables. (The configuration energies can be given relative to the ground state of the atom.)

(a) C, $1s^2 2s^2 2p^2$;

(b) N, $1s^2 2s^2 2p^3$;

(c) N, $1s^2 2s^2 2p^2 3s$.

12. Explain why the second ionization potential of lithium, for the process $Li^+ \rightarrow Li^{2+} + e^-$, is less than that predicted for a hydrogenlike atom with $Z = 3$.

13. Consider the effect of the nuclear charge on the importance of relativistic effects in atoms, first by estimating from a Bohr model the velocity of a $1s$ electron in an atom of lead. The effective mass of a particle with rest mass m and speed v is $m' = m/\sqrt{1 - (v^2/c^2)}$. What is v/c for a $1s$ electron of Pb? What is its effective mass, based on the simple expression above for m'? What velocity v' does one obtain if one carries out the Bohr calculation with the above expression for m', instead of a velocity-independent m?

14. The outer electron of an alkali atom may be treated in an approximate way, as if it were in a hydrogenic orbital. Suppose that one takes the quantum number for the outer electron to be 2, 3, 4, 5, and 6, respectively, for Li, Na, K, Rb, and Cs. What values must Z be given to account for the observed first ionization potentials of these atoms? Explain why they differ from unity.

15. Use the Pauli exclusion principle and Hund's rules to find the number of unpaired electrons and the term of lowest energy for the following atoms:

(a) P

(b) S

(c) Ca

(d) Br

(e) Fe

16. Hydrogen atoms are placed in a strong magnetic field and excited; their emission spectrum is recorded under conditions of moderately high resolution (0.1 cm^{-1} or better). What is the appearance of the portion of the spectrum due to H($3p$) $\rightarrow$ H($2s$) transitions, and how does it differ from the spectrum of the same transition in the absence of a magnetic field?

17. Show that the lowest configuration of the nitrogen atom, $1s^2 2s^2 2p^3$, gives rise to the terms ^2D, ^2P, and ^4S.

18. Derive the terms of the configuration $1s^2 2s^2 2p^6 3s^2 3p 3d$, of the silicon atom.

19. Explain this observation: The energy difference between $1s^2 2s$, $^2S_{1/2}$ and $1s^2 2p$, $^2P_{1/2}$ states of Li is 14904 cm^{-1}, whereas that between the $2s$, $^2S_{1/2}$ and $2p^2$, $P_{1/2}$ states of Li^{2+} is only 2.4 cm^{-1}.

20. The first excited state (and higher excited states as well) of He exhibits a positive electron affinity, although the electron affinity of He in its ground state is negative.

(a) What are the configuration and term designations of the first two excited states of the helium atom?

(b) What is the configuration and term designation of the lowest-energy bound state of the negative ion He$^-$? Note that this cannot be the same as any state built by adding an electron to He in its ground state.

(c) Interpret why atoms in excited configurations generally have positive electron affinities, whereas atoms in closed-shell ground-state configurations seem to have only negative electron affinities.

21. What are the lowest terms for the ions Ti^{2+}, Mn^{2+}, and Fe^{3+}, if the first two electrons to be lost by the corresponding neutrals are the two $4s$ electrons? What are the possible values of the quantum number J for each of these ions?

22. What J values are possible for the ^3P, ^1D, and ^1S states of the silicon atom? Look up the observed splittings of these states in C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards Circular 467) and estimate the spin–orbit splitting parameter ζ for as many of these states as the data permit.

23. Given the following data:

	Li	Na	K	Rb	Cs	Fr
Z	3	11	19	37	55	87
Atomic weight	6.94	23.00	39.10	85.47	132.91	?
Density (g/cm^3)	0.53	0.97	0.86	1.53	1.90	?
Atomic volume (cm^3)	13.0	23.7	45.5	55.9	70.0	?
Melting point (°C)	186	97.5	62.3	38.5	26	?
Boiling point (°C)	1200	880	760	700	670	?

Predict the numerical values for the atomic weight, density, atomic volume, melting and boiling points of francium, element number 87. What will be its characteristic chemical properties?

24. Show from Eqs. 5.26 and 5.27 that the energy associated with spin–orbit interaction is

$$E_{so} = \tfrac{1}{2} \zeta \hbar^2 [J(J+1) - L(L+1) - S(S+1)].$$

25. (Difficult) Substitute $\psi^{(1)}$ of Eq. 5.12 and $\psi^{(2)}$ of Eq. 5.13 into the expression for the expectation value of the energy, Eq. 5.11, and show that the corresponding values given in the text, -74.83 eV and -77.49 eV, respectively, are correct.

26. Electronic structure calculations can be performed using readily available software packages. (One such package, available free of charge from Iowa State University, is GAMESS, Generalized Atomic and Molecular Electronic Structure System—see http://www.msg. ameslab.gov/GAMESS/GAMESS.html.) A popular calculational method is the Hartree–Fock Self-Consistent Field (HF–SCF) calculation with each atomic orbital being represented as a linear combination of Gaussian basis functions of the form e^{-r^2}. A variety of basis sets are available.
    (a) In a minimal basis STO–NG calculation, each atomic orbital is represented by one Slater type orbital of the form e^{-r}, which is itself composed of N Gaussians.
    (b) In an m–npG basis set calculation, each inner shell atomic orbital is represented as one linear combination of m Gaussians. Each valence shell atomic orbital is represented by two basis functions, a linear combination of n Gaussians and a linear combination of p Gaussians.

    Compute the Hartree–Fock ground electronic state energy of atomic hydrogen using the following basis sets: (a) STO–3G; (b) 3–21G; (c) 6–31G. Note for hydrogen that there are no inner shell orbitals. Compare the computed orbital energy to the exact ionization energy of the hydrogen atom in its electronic ground state.

27. Compute the Hartree–Fock energy of the ground electronic state of the He atom using the (a) STO–3G, (b) 3–21G, and (c) 6–31G basis sets and the HF–SCF method. Compare these calculated energy values to the experimental value of -78.99 eV.

28. Repeat Problem 5.27 for the C atom in its ground electronic state, computing the 1–electron orbital energies (the eigenvalues corresponding to the α and β sets of eigenvectors reported by GAMESS). Compare the least-negative eigenvalue with the experimental first ionization energy (Koopman's Theorem).

29. Repeat Problem 5.27 +2 for the O atom in its ground electronic state.