CHAPTER 9

Angular momentum

Classically, angular momentum is the cross product of the position vector with the momentum vector of a particle

L = r x p

where L, r, and p are vectors. There are operators for L_x, L_y, and L_z, the components for the angular momentum vector along the x, y, and z axes, in both Cartesian coordinates and spherical polar coordinates, as discussed in the Chapter 8 handout. Note that

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$$

$$[L_x, L_y] = i\hbar L_z \quad [L_y, L_z] = i\hbar L_x \quad [L_z, L_x] = i\hbar L_y$$

The significance of the above, among other things, is that it is possible to find a set of functions that are simultaneously eigenfunctions of L^2 and one of the three components of the angular momentum vector. Because the operator for L_z in spherical polar coordinates is more simple than those for L_x and L_y ($L_z = - i\hbar \, \partial/\partial\phi$), we usually choose to work with functions that are eigenfunctions of L^2 and L_z (the spherical harmonics).

Central potential problems and the spherical harmonics

A central potential is one where the potential energy at most depends only on r, the distance between a particle and the center of our coordinate system. In spherical polar coordinates, this means V = V(r), that is, that the potential energy is independent of the angles θ and φ. For any three dimensional problem where the potential energy is angle independent, we can show that the TISE for the system separates into an equation for the radial dependence of the wavefunction R(r), and a function for the angular dependence of the wavefunction F(θ,φ). Further, the solutions to the angular part of the TISE are always the same set of functions, the spherical harmonics (so F(θ,φ) = $Y_{\ell,m\ell}(θ,φ)$). This means that for any central potential TISE, the only new part of the equation is the solution for the radial functions R(r).

The TISE for the hydrogen atom

For the hydrogen atom (and assuming the center of our coordinate system is the center of the nucleus), the potential energy is

$$V(r) = - \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{r}$$

where Z is the charge of the nucleus, e is the fundamental unit of charge, $4\pi\varepsilon_0$ is a conversion factor that makes V have MKS energy units (Joules), and r is the distance between the nucleus and the electron. We have written the expression for V(r) in terms of Z because the solution to the TISE for a hydrogen atom (Z = 1) will also be a solution to any atomic ion possessing a single electron (so He^+, Li^{2+}, …). Since V = V(r), this is an example of a central potential problem, and so the solutions to the angular part of the TISE for the hydrogen atom are the spherical harmonics. The radial solutions can be found by standard methods (see the Chapter 8 handout), and are in terms of associated Laguerre polynomials. The overall solutions to the TISE can be written as

$$\Psi_{n,\ell, m\ell}(r,\theta,\phi) = R_{n,\ell}(r) \, Y_{\ell,m\ell}(\theta,\phi)) \quad \text{where} \quad \begin{array}{l} n = 1, 2, 3, \dots \\ \ell = 0, 1, 2, \dots (n-1) \\ m_\ell = 0, \pm1, \pm2, \dots, \pm\ell \end{array}$$

The functions R(r) and Y(θ,ϕ) are individually normalized, so that

$$1 = \int_0^\infty r^2 \, R^*(r) \, R(r) \, dr \qquad\qquad 1 = \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \, Y^*(\theta,\phi) \, Y(\theta,\phi)$$

Note that the above integrals contain <u>integration factors</u> (r^2 dr for the radial wavefunction and sinθ dθ dϕ for the angular wavefunctions) to account for the differences between Cartesian coordinates and spherical polar coordinates. The radial wavefunctions are real functions, and so $R^*(r) = R(r)$, and complex conjugation doesn't matter. The spherical harmonics are in general complex functions, and so we need to remember how to write $Y^*(\theta,\phi)$. Expectation values for operators are found as before. However, for an expectation value for a quantity that only depends on r, we only need to work with the radial solutions to the TISE. For example

$$<r> = \int_0^\infty r^2 \, R^*(r) \, r \, R(r) \, dr$$

Probabilty is also found as before, though we again need to take into account the integration factors.

$$P(r) \, dr = r^2 \, |R(r)|^2 \, dr$$

If we are interested in the probability of an electron being found between a and b (a < r < b), that will be

$$P(a < r < b) = \int_a^b P(r) \, dr = \int_a^b r^2 \, |R(r)|^2 \, dr$$

We can find the most probable value for r by the usual method for finding extreme points

$$\partial/\partial r \, P(r) = 0$$

Note however that this will identify all of the extreme points for P(r) (minima and local maxima) so some care needs to be used in finding r_{mp}.

The number of radial nodes for R(r) (and also for P(r)) is

radial nodes = $(n - \ell) - 1$

The eigenvalues for the TISE for the hydrogen atom are (assuming an infinitely massive nucleus)

$$E_n(\text{in Joule}) = - \frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2} \frac{1}{n^2} = - \frac{R_\infty}{n^2} \qquad R_\infty = 2.1798 \times 10^{-18} \text{ J}$$

$$E_n(\text{in cm}^{-1}) = - \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} \frac{1}{n^2} = - \frac{R_\infty}{n^2} \qquad R_\infty = 109737. \text{ cm}^{-1}$$

The above values assume an infinitely massive nucleus. For a real nucleus, we should replace m_e with μ (reduced mass)

$$\mu = \frac{m_e \, m_N}{(m_e + m_N)}$$

where m_e is the mass of the electron and m_N is the mass of the nucleus. For a ^{1}H atom (normal isotope of hydrogen) the Rydberg constant (written as R_H) is $R_H = 2.1786 \times 10^{-18}$ J and $R_H = 109677.$ cm^{-1}, slightly different than the values for R_∞.

Radial wavefunctions are often written in terms of a_0, the Bohr radius, and ρ

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = 0.0529 \text{ nm} \qquad\qquad \rho = \frac{2Zr}{na_0}$$

where n is the principle quantum number and Z is the charge of the nucleus.

Because the spherical harmonics are in general complex functions, they are often rewritten in such a way as to produce an equivalent set of real wavefunctions. For example, the $\ell = 1$ spherical harmonics can be replaced with the real functions p_x, p_y, p_z. This is convenient both for visualizing the appearance of the angular solutions to the TISE for hydrogen and for calculational chemistry. The method for constructing the p_x and p_y orbitals from the $\ell = 1$, $m_\ell = \pm 1$ is discussed in the Chapter 9 handout.

Selection rules for hydrogen atoms

Absorption or emission of light by an atom, molecule, or ion must satisfy conservation of energy. However, some energetically allowed transitions are not observed, or are weakly observed, while others are strong transitions. This can often be attributed to selection rules that list conditions that a transition must satisfy to be allowed (and so expected to occur). Transitions that violate one or more of the selection rules are called forbidden transitions, and are expected to be either weak or not present.

Selection rules are obtained by looking at simplified solutions to the TISE for systems (often by symmetry arguments), usually in the dipole approximation. In this approximation, the charges in in a system are used to construct a dipole moment operator

$$\mu = \Sigma_{i=1}^{N} q_i\, r_i$$

where q_i is the charge of the ith particle and r_i is the vector giving the location of the particle in space. The intensity of a transition is

$$I \sim | \int \Psi^*_f\, \mu\, \Psi_i\, d\tau |^2$$

where Ψ_f and Ψ_i are the wavefunctions for the final and initial states of the system, μ is the dipole operator, and $d\tau$ indicates integration over all of the coordinates of the system. While evaluating the integral in the exprsssion for I is usually difficult, symmetry arguments can often be used to determine whether or not the integral is equal to zero. For cases where the integral is equal to zero we have a forbidden transition, while for cases where the integral is not equal to zero we have an allowed transition. The selection rules are not rigorous, but they are useful in identifying strong (allowed) and weak (forbidden) transitions in systems.

The selection rules for absorption or emission of light by hydrogen atoms are as follows

$$\Delta n = \text{anything} \qquad\qquad \Delta \ell = \pm 1 \qquad\qquad \Delta m_\ell = 0, \pm 1$$

Because we can find combinations of ℓ and m_ℓ that will satisfy the above selection rules for any initial and final values for n, all transitions between the energy states of hydrogen can be observed in absorption or emission. Emission spectra with $n_f = 1$ are called the Lymen transitions (and occur in the UV region) and those with $n_f = 2$ are called the Balmer transitions (and occur in the visible region). Transitions with $n_f > 2$ occur in the IR region and are also observed in absorption and emission.

Electron spin

In the TISE for hydrogen (and other systems containing electrons) electron spin is added to the solutions as an additional pair of quantum numbers s and m_s, with $s = \frac{1}{2}$ and $m_s = \pm \frac{1}{2}$ (by convention $m_s = + \frac{1}{2}$ is called "spin up" and $m_s = - \frac{1}{2}$ is called "spin down".)

Electrons in an atom, molecule, or ion are required to satisfy the Pauli principle, which states that no two electrons in the system can have the same set of quantum numbers. The Pauli principle is itself a consequence of a symmetry requirement for the wavefunction representing a collection of identical particles, as discussed in the Chapter 9 handout.

Multi-electron atoms

For atoms or ions with more than one electron the Hamiltonian for the system can be broken down into three terms

$$H = T_e + V_{Ne} + V_{ee}$$

where

$T_e = - (\hbar^2/2m_e) \Sigma_{i=1}^{N} \nabla_i^2$ \qquad\qquad electron kinetic energy

$V_{ne} = - (Ze^2/4\pi\varepsilon_0) \Sigma_{i=1}^{N} (1/r_i)$ \qquad\qquad nuclear-electron potential energy

$V_{ee} = (e^2/4\pi\varepsilon_0) \Sigma_{i=1}^{N} \Sigma_{j>i}^{N} (1/r_{ij})$ \qquad\qquad electron-electron potential energy

The last term, V_{ee}, is not present in a one electron system. It is the presence of V_{ee} that makes it impossible to find an exact solution to the TISE for a multielectron atom or atomic ion.

While an exact solution to the TISE for a multielectron atom or atomic ion cannot be found, good approximate solutions can be obtained. This is usually done in the orbital approximation

$$\Psi(r_1, r_2, \ldots, r_N) = \psi(r_1)\psi(r_2)\ldots\psi(r_N)$$

where r_1, r_2, … are vectors indicating the position of each electron in spherical polar coordinates in a system where the nucleus is at the center of the coordinate system. The orbital approximation allows us to assign a set of quantum numbers n, ℓ, m_ℓ, m_s to each electron.

The ground state electron configuration for an atom can be found using the Pauli principle (no two electrons can have the same set of quantum numbers) and the Aufbau principle (electrons add to the lowest energy available orbital). The normal order for adding electrons, exceptions to the general rules for finding ground state electron configurations, and the procedure for find electron configurations for atomic ions are taught in general chemistry and reviewed in Atkins.

It is possible to arrange electrons in a configuration corresponding to higher energy states of the system. For example, for the carbon atom

C $1s^2\, 2s^2\, 2p^2$ \qquad (ground state electron configuration)

C $1s^2\, 2s^1\, 2p^3$ \qquad (an excited electron configuration)
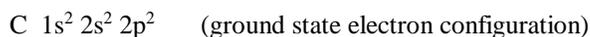
There are often different electronic states associated with a particular electron configuration, each with its own value for energy. The different electronic states are indicated by a term symbol of the form

$$^{2S+1}L_J$$

where S is the total spin angular momentum, L is the symbol for the total orbital angular momentum (L = 0 is an S state, L = 1 is a P state, L = 2 is a D state, and so forth) and J is a quantum number that accounts for spin-orbit coupling. Since the effect of spin orbit coupling for atoms from the first few rows of the periodic table is small, the different possible J states for an electronic state are sometimes not indicated.

The electronic states for an atom are usually degenerate. The degeneracies are as follow

Spin degeneracy $g_S = 2S + 1$ (the different values for M_S for a particular value of S)

Orbital degeneracy $g_L = 2L + 1$ (the different values for m_L for a particular value of L)

Spin-orbit degeneracy $g_J = 2J + 1$ (the different values for M_J for a particular value for J)

For an electronic state with a value of L for the orbital quantum number and S for the spin quantum number, the total degeneracy of the state (ignoring spin-orbit coupling) is $g_{LS} = (2L + 1)(2S + 1)$.

The general method for identifying the possible electronic states for a particular electron configuration is given in the Chapter 9 handout. The handout also discusses Hund's rules, which allow us to order the electronic states corresponding to a particular electron configuration from lowest to highest energy.

Atomic spectroscopy

The selection rules for allowed and forbidden transitions between the electronic states of an atom can be used to predict where the atom should have strong absorption or emission of light. If the energies of the electronic states are knows they can be used along with the selection rules to predict the wavelengths at which an atom will absorb or emit light. Selection rules and their use are discussed in the Chapter 9 handout.

CHAPTER 10

Approximation methods for solving the TISE

Because the TISE for most systems, including those of greatest interest to chemists, do not have exact solutions, several methods for finding approximate solutions to a TISE have been developed. For small systems these approximate solutions are essentially exact (that is, the difference between the approximate solution and the exact solution is negligible). Even when this is not the case, the approximate solutions for a TISE are often of sufficient quality that the properties of the system can be discussed.

The two common approximation methods used to find solutions to a TISE are perturbation theory and variation theory. In perturbation theory the Hamiltonian for a system is written as $H = H_0 + \lambda H_1$, where H_0 is a part of the total Hamiltonian that has an exact (or high quality approximate) solution, and H_1 is the part of the Hamiltonian that makes finding an exact solution difficult or impossible (the perturbation). λ is a parameter that can have values between 0 and 1, and is used to turn off the perturbation ($\lambda = 0$) or allow the perturbation to grow in strength until it reaches its full value ($\lambda = 1$). Standard methods are used to determine the effect of the perturbation on the wavefunctions and energies of the system. Variational theory makes use of the variational theorem, which states that for any normalizable and well behaved function f, the energy corresponding to that function, E_f, given by the expression

$$E_f = \int f^* \, H \, f \, d\tau$$

must be laerger than or equal to E_0, the energy of the ground state of the system. This is useful because it means any modification of f that lowers the value for E_f brings us closer to the true ground state energy of the system.

Perturbation theory and variational theory are discussed further in the Chapter 10 handout.

Valence bond theory

One simple method for modeling bonding in molecules or molecular ions is valence bond theory. In valence bond theory a covalent bond is formed between atoms A and B by combining an atomic orbital on each atom, each of which contains an electron. In this case

$$\Psi_{VB} = N \{ \psi_A(1)\psi_B(2) \pm \psi_A(2)\psi_B(1) \}$$

where the "+" combination lowers the energy corresponds to the formation of a valence bond. Valence bond theory can also include combinations of atomic orbitals that place both electrons on the same atom, which can be used to account for unequal sharing of electrons in polar bonds.

A process called hybridization can be used as an intermediate step to construct new orbitals that are more useful in forming valence bonds than the original atomic orbitals. The various pure hybridizations are indicated by the identity of the atomic orbitals used to construct the hybrid orbitals (and so sp, sp^2, sp^3, sp^3d, and sp^3d^2 for the most common pure hybrid orbitals). By changing the amounts of the atomic orbitals used to construct hybrid orbitals, bond angles different than those found in the pure cases can be found. For example, two sp^3 hybrid orbitals can be formed with a bond angle of 105 °, instead of the 109.5 ° found in pure sp^3 hybridization, to account for the H-O-H bond angle observed in the water molecule.

Valence bond theory also includes a concept called resonance, where the actual bonding in a molecule or ion is given by a combination of several valence bond structures. In some cases, such as benzene, the different resonance structures contribute equally to the bonding, while in other cases different resonance structures make different contributions to the bonding. In all cases, the bonding is an average of the resonance structures, with the average representing the bonding taking place.

The TISE for a molecule and the Born-Oppenheimer approximation

The Hamiltonian operator for a diatomic molecule AB with N electrons can be written as follows

$$H = T_N + T_e + V_{NN} + V_{Ne} + V_{ee}$$

where

$T_n = - [(\hbar^2/2m_A) \nabla_A^2 + (\hbar^2/2m_B) \nabla_B^2]$ nuclear kinetic energy

$T_e = - (\hbar^2/2m_e) \Sigma_{i=1}^N \nabla_i^2$ electron kinetic energy

$V_{ne} = - [(Z_Ae^2/4\pi\varepsilon_0) \Sigma_{i=1}^N (1/r_{Ai}) + (Z_Be^2/4\pi\varepsilon_0) \Sigma_{i=1}^N (1/r_{Bi})]$ nuclear-electron potential energy

$V_{nn} = (Z_AZ_Be^2/4\pi\varepsilon_0) (1/r_{AB})$ nuclear-nuclear potential energy

$V_{ee} = (e^2/4\pi\varepsilon_0) \Sigma_{i=1}^N \Sigma_{j>i}^N (1/r_{ij})$ electron-electron potential energy

A similar division of therms can be used to write the Hamiltonian operator for a molecule or molecular ion with three or more atoms.

The TISE corresponding to the above Hamiltonian operator does not have an exact solution. It can, however, be simplified a bit by making the Born-Oppenteimer approximation. The approximation is based on the observation that atomic nuclei have large masses compared to the mass of an electron, and so can be assumed to move solyly in comparison to the electron moton. The nuclei are therefore assumed to be stationary, and the TISE is solved for a particular value for bond distance. The bond distance is then changed and the TISE solved for the new value. This process is carried out for a range of bond distances to construct a potential energy curve.

Making the Born-Oppenheimer approximation is equivalent to dropping the T_N term from the Hamiltonian, and making the V_{NN} term equal to a constant. Even with these simplifications the TISE cannot be solved exactly, but there are methods that have been developed to carry out calculations that result in good approximations to the exact solution to the TISE when the Born-Oppenheimer approximation is made. Note that when there are more than two atoms the approximate solutions result in a potential energy surface in $3N - 5$ or $3N - 6$ dimensions, which is difficult to picture but which can be used in the same way as a potential energy curve for a diatomic molecule.

LCAO-MO

A simple method for carrying out calculations on a molecule is called LCAO-MO (Linear Combinations of Atomic Orbitals to form Molecular Orbitals). A great advantage of LCAO-MO is that it allows one to discuss bonding in molecules in a simple and pictorial way.

In the LCAO-AO method we proceed as follows:

1) Used the AOs (atomic orbitals) for the atoms to construct molecular orbitals
2) Use the Pauli principle and the Aufbau proinciple to add electrons to the MOs and obtain a ground state electron configuration (or rearrange the electrons to find excited state electron configurations).
3) For each electron configuration find the possible electronic states.

LCAO-MO for H_2

The LCAO-MO procedure applied to the hydrogen molecule (and related molecules or ions) uses the 1s atomic orbitals on the two hydrogen atoms (H_A and H_B) to form two molecular orbitals

$$\sigma_{1sg} = N_+ \{ \psi_{1sA} + \psi_{1sB} \} \qquad\qquad \sigma_{1su}* = N_- \{ \psi_{1sA} - \psi_{1sB} \}$$

Note that for a homonuclear diatomic molecule the MOs can be classified as g (gerande) if the wavefunction does not change sign when inverted throught the center of the molecule, or u (ungerande) if the wavefunction does change Δsign upon inversion. Also note that MOs that raise the energy are labeled with a "*" and called antibonding orbitals, while those that lower the energy are called bonding orbitals, and are not labeled.

We can write electron configurations for the ground and excited states of molecules and ions in the same way as done for atoms. For example

H_2	$(\sigma_{1sg})^2$	ground state electron configuration for the H_2 molecule
H_2	$(\sigma_{1sg})^1 (\sigma_{1su}*)^1$	an excited state electron configuration for the H_2 molecule
H_2^-	$(\sigma_{1sg})^2 (\sigma_{1su}*)^1$	ground state electron configuration for the H_2^- ion

Note that the overall symmetry for the wavefunction for a homonuclear diatomic molecule will be either g or u, and can be found using the symmetries for each electron. Note also that g x g = u x u = g, and that g x u = u x g = u.

We can also define a bond order for a molecule or ion. Since a covalent bond is formed from the sharing of a pair of electrons, the bond order for a particular electron configuration is

$$\text{Bond order} = \frac{(\# \text{ bonding e}^- - \# \text{ antibonding e}^-)}{2}$$

In the above examples the bond order is 1 for the ground state electron configuration of H_2, 0 for the excited state electron configuration of H_2, and 1/2 for the electron configuration of H_2^-.

As is the case for atoms, term symbols can be written for the electronic states corresponding to the electron configuration of a diatomic molecule or ion. The general form for the term symbol is

$$^{2S+1}\Lambda_{g/u}{}^{+/-}$$

In this term symbol S is the quantum number for the toal electron spin and Λ is the symbol for the value for the orbital angular momentum around the z-axis, chosen to be in the same direction as the bond between the two atoms. Note that $\Lambda = 0$ is an Σ state, $\Lambda = 1$ is a Π state, and $\Lambda = 2$ is a Δ state.
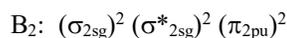
LCAO for homonuclear second row diatomics

The LCAO-MO method can be extended to account for bonding in larger diatomic molecules. Since bonding usually only involves the valence electrons of an atom, only atomic orbitals for valence electrons are used to construct molecular orbitals. Molecular orbitals are formed from the 2s and 2p atomic orbitals in the same way as for the H_2 molecule, leading to a set of bonding and antibonding molecular orbitals. The normal ordering of these orbitals in terms of energy is given below, and applies for diatomic molecules Li_2 to N_2 (along with their cations and anions). For O_2, F_2, and Ne_2 (and their ions) the only difference in the ordering of the energy levels is that the σ_{2pg} molecular orbital is lower in energy than the π_{2pu} orbitals.

MO Diagram for Li_2 through N_2
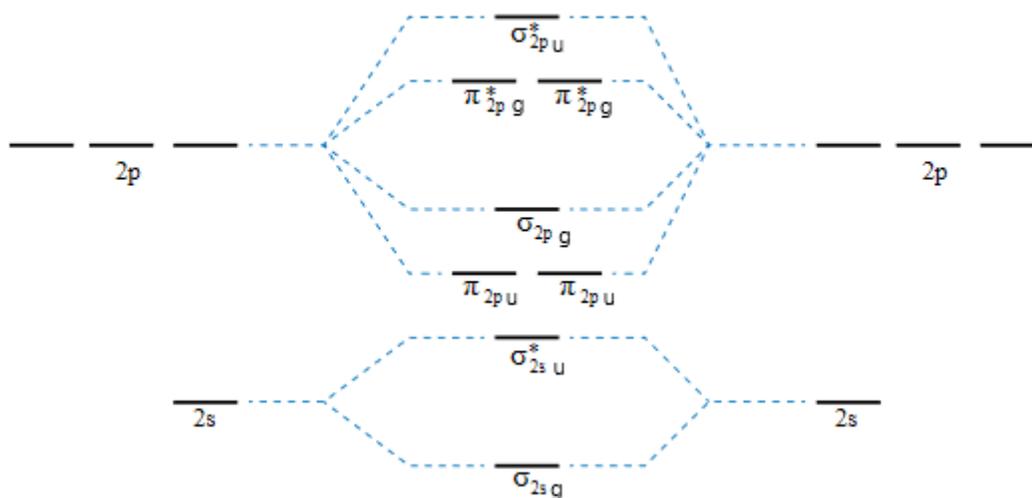
As for the H_2 molecule, electron configurations can be written for the ground and excited state arrangement of electrons for a period two homonuclear diatomic molecule. For example, for the B_2 molecule

$$B_2: \ (\sigma_{2sg})^2 \ (\sigma^*{}_{2sg})^2 \ (\pi_{2pu})^2$$

The bond order and term symbols for the different possible electronic states for a particular electron configuration can be found, as discussed in the Chapter 10 handout.

LCAO for heteronuclear second row diatomics

The LCAO-MO method also applies to second row heteronuclear diatomic molecules and their ions. There are two differences between homonuclear and heteronuclear diatomic molecules. First, the initial energies of the atomic orbitals for the different atoms in a heteronuclear diatomic molecule are not the same. For example, in the CO molecule, the 2s and 2p atomic orbitals for the oxygen atom are slightly lower in energy than those for the carbon

atom (as a result of the larger charge of the nucleus in the oxygen atom). Because of this, the molecular orbitals that form do not contain equal amounts of atomic orbitals from the two atoms. Instead, the atom whose AO is closer in energy to the MO contributes more to the molecular orbitals that forms. Second, g/u symmetry no longer applies for a heteronuclear diatomic molecule because inverting the molecule through its center interchanges the two atomic nuclei, which are for different atoms, and so is no longer an element of symmetry.

As is the case of homonuclear diatomic molecules electron configurations for different arrangements of electrons can be found. Bond orders and the term symbols for these states can also be obtained, as discussed in the Chapter 10 handout.

Spectroscopy and selection rules

The selection rules for allowed and forbidden transitions in diatomic molecules are discussed in the Chapter 10 handout.