The Helium Atom

The quantum mechanical treatment of the hydrogen atom and hydrogen-like atoms is impressive. It provides an **exact** account of the energy levels, angular momentum, electronic spectra, electron densities, *etc*.

The next system to study is clearly helium, a two-electron atom.

Using *M* for the mass of the helium nucleus and subscripts 1 and 2 for the two electrons, gives

the Hamiltonian operator for the helium atom

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0\left|\vec{R}-\vec{r}_1\right|} - \frac{2e^2}{4\pi\varepsilon_0\left|\vec{R}-\vec{r}_2\right|} + \frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_2-\vec{r}_1\right|}$$

In this equation, $\vec{R}$ is the position of the nucleus, ∇_1^2 and ∇_2^2 are the Laplacian operators with respect to the coordinates of electron 1 and 2, and $\vec{r}_1$, $\vec{r}_2$ are the positions of the electrons.

The Schrödinger equation to be solved is

$$\hat{H}\psi(\vec{R},\vec{r}_1,\vec{r}_2) = E\psi(\vec{R},\vec{r}_1,\vec{r}_2)$$

Some simplification is possible by transforming to the center-of-mass coordinates. Because $M >> m_e$, it is an excellent approximation to regard the helium nucleus as stationary. Fixing the nucleus at the origin of the spherical coordinates gives the

the Schrödinger equation for the helium atom

$$-\frac{\hbar^2}{2m_e}(\nabla_1^2+\nabla_2^2)\psi(r_1,r_2) - \frac{2e^2}{4\pi\varepsilon_0}(\frac{1}{r_1}+\frac{1}{r_2})\psi(r_1,r_2) + \frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_2-\vec{r}_1\right|}\psi(r_1,r_2) = E\psi(r_1,r_2)$$

Unfortunately, even the simplified Schrödinger equation ***cannot be solved exactly***. This is not a surprise. The helium atom is a three-body problem: two electrons plus the helium nucleus. Three-body problems, even in classical physics, cannot be solved analytically.

The culprit is the term

$$\frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_2-\vec{r}_1\right|}\psi(r_1,r_2)$$

If this term was not present, then Schrödinger's equation would be the sum of two Schrödinger's equations for hydrogen-like atoms, in which case the wave function would be simply the product of two hydrogen atomic orbitals, one for each electron.

The troublesome $e^2/4\pi\varepsilon_0\left|\vec{r}_2-\vec{r}_1\right|$ term is called the **interelectron repulsion term**. It represents the positive potential energy for the interaction of the two electrons. The electrons are constantly moving, so the distance $\left|\vec{r}_2-\vec{r}_1\right|$ between them is constantly changing.

An obvious possibility is to neglect the $e^2/4\pi\varepsilon_0\left|\vec{r}_2-\vec{r}_1\right|$ term, and hope that its effects are small! This simple-minded approach, the **complete neglect of interelectron repulsion**, gives a calculated energy of -1.7438×10^{-17} J (–10,501 kJ per mole) for the ground state helium atom, compared to the experimental value -1.2657×10^{-17} J (–7,622.0 kJ per mole, smaller by 27 %). Qualitatively, does this make sense?

Neglecting interelectron repulsion produces an error of –2,880 kJ per mole. This error is of course unacceptably large.

Approximate Solutions of Schrödinger's Equation for the Helium Atom

The example of the helium atom illustrates that it is not possible to solve Schrödinger's equation for something as "simple" as a two-electron atom! At first glance, this might appear to render quantum mechanics useless for systems of interest to chemists and

physicists. Fortunately, powerful numerical methods are available to solve Schrödinger's equations to almost any desired degree of accuracy, given enough time and adequate computer facilities.

1. Perturbation ("Successive Approximation") Methods

The helium atom can be used to illustrate a numerical procedure for solving the Schrödinger's equation called **"perturbation theory"**. In fact, we have already used perturbation theory, without knowing it, in the analysis of the Zeeman effect, when an applied magnetic field produces small changes in atomic energy levels.

The basic idea behind perturbation methods is simple: start with the wave function and the energy known for a closely related (but simpler) problem for which Schrödinger's equation has been solved exactly, then calculate correction terms ("perturbations") to be applied to give more accurate values for the wave functions and energies for the system under consideration.

For the helium atom, the equation to be solved is

$$\hat{H}\psi = E\psi$$

The total Hamiltonian in this case can be expressed as the sum of the Hamiltonians for two hydrogen atoms $\hat{H}^{(0)}$ and the interelectron repulsion $\hat{H}^{(1)}$.

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$$

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\varepsilon_0}(\frac{1}{r_1} + \frac{1}{r_2}) \qquad \text{(for two H atoms)}$$

$$\hat{H}^{(1)} = \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_2 - \vec{r}_1|}$$

Notice that the Schrödinger equation $\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$ for hydrogen atoms has been solved exactly, so $\psi^{(0)}$ and $E^{(0)}$ are known.

$\hat{H}^{(1)}$ is assumed to a smaller "correction term", so we write

$$\psi = \psi^{(0)} + \Delta\psi$$

$$E = E^{(0)} + \Delta E$$

and assume that $\Delta\psi$ and ΔE are also small. If these quantities can be evaluated, then corrections can be applied to $\psi^{(0)}$ and $E^{(0)}$ to allow for electron repulsion to give a more accurate quantum mechanical description of the He atom.

At the level of approximation used here, Schrödinger's equation $\hat{H}\psi = E\psi$ is

$$(\hat{H}^{(0)} + \hat{H}^{(1)})(\psi^{(0)} + \Delta\psi) = (E^{(0)} + \Delta E)(\psi^{(0)} + \Delta\psi)$$

Multiplying through gives the terms

$$\hat{H}^{(0)}\psi^{(0)} + \hat{H}^{(1)}\psi^{(0)} + \hat{H}^{(0)}\Delta\psi + \hat{H}^{(1)}\Delta\psi = E^{(0)}\psi^{(0)} + \Delta E\psi^{(0)} + E^{(0)}\Delta\psi + \Delta E\Delta\psi$$

This equation looks very complicated! But we know that $\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$, so the first terms on the left and right sides of the equation cancel. Also, we can neglect the second-order products $\hat{H}^{(1)}\Delta\psi$ and $\Delta E\Delta\psi$ of small correction terms and obtain

$$\hat{H}^{(1)}\psi^{(0)} + \hat{H}^{(0)}\Delta\psi = \Delta E\psi^{(0)} + E^{(0)}\Delta\psi \qquad (1)$$

This result is called a **"first-order" perturbation equation** because all of the terms are first-order in the correction terms $\hat{H}^{(1)}$ and ΔE.

It is not obvious, but equation (1) can be simplified further. Multiplying both sides from the left by the complex conjugate $\psi^{(0)*}$ and integrating over all space gives

$$\int \psi^{(0)} * (\hat{H}^{(0)} - E^{(0)}) \Delta\psi \, \mathrm{d}\tau + \int \psi^{(0)} * \hat{H}^{(1)} \psi^{(0)} \, \mathrm{d}\tau = \Delta E \int \psi^{(0)} * \psi^{(0)} \, \mathrm{d}\tau$$

The integral on the right side of this equation is unity because $\psi^{(0)}$ is normalized. More importantly, the first integral on the left side of this equation is zero! To demonstrate this result, recall that $\hat{H}^{(0)} - E^{(0)}$ is Hermitian, and consequently

$$\int \psi^{(0)} * (\hat{H}^{(0)} - E^{(0)}) \Delta\psi \, \mathrm{d}\tau = \int \Delta\psi [(\hat{H}^{(0)} - E^{(0)}) \psi^{(0)}]^* \, \mathrm{d}\tau$$

This integral vanishes because $\hat{H}^{(0)} \psi^{(0)} = E^{(0)} \psi^{(0)}$.

We obtain the relatively simple expression

$$\boxed{\Delta E = \int \psi^{(0)} * \hat{H}^{(1)} \psi^{(0)} \, \mathrm{d}\tau}$$

for the first-order energy correction (*does it make sense?*) and the

first-order perturbation expression for the energy

$$\boxed{E = E^{(0)} + \Delta E = E^{(0)} + \int \psi^{(0)} * \hat{H}^{(1)} \psi^{(0)} \, \mathrm{d}\tau}$$

Application of Perturbation Theory to the He Atom The integration is a bit lengthy, but it can be done analytically, and it gives the calculated energy $E^{(0)} + \Delta E = -1.198 \times 10^{-17}$ J (–7220 kJ per mole) for the ground state helium atom, compared to the experimental value -1.2657×10^{-17} J (–7622.0 kJ per mole), which is smaller by about 5 %. This error (402 kJ per mole) is an encouraging order of magnitude smaller than the error –2879 kJ per mole obtained (–38 % error) in the energy –10,501 kJ by complete neglect of interelectron repulsion, but still unacceptably large.

For a more accurate estimation of the energy of the helium atom, we could evaluate second-order corrections to $E^{(0)} + \Delta E$, $\psi^{(0)} + \Delta\psi$, and so on. *Thirteenth-order* (*!*) perturbation theory (C. W. Scheer and R. E. Knight, *Rev. Mod. Phys.* **1963**, *35*, 426) gives -1.2657×10^{-17} J for the energy of the helium ion, in perfect agreement with experiment.

2. Variational Methods

Perturbation methods are widely used in quantum mechanical calculations. Important examples include the effects of anharmonicity and applied electric or magnetic fields. Perturbation calculations require, however, Schrödinger's equation to have been already been solved ***exactly*** for a similar problem. This can be a serious limitation.

A completely different and more general method for finding approximate solutions to Schrödinger's equations is based on the following theorem:

> If E_0 is the lowest (ground state) eigenvalue of the Hamiltonian operator $\hat{H}$ and φ is a trial wave function (not necessarily normalized) for the operator, then

$$\boxed{\frac{\int \varphi^* \hat{H} \varphi \, d\tau}{\int \varphi^* \varphi \, d\tau} \geq E_0}$$

Variational Theorem

Application of the variational theorem is simple in principle. A **trial function χ** is chosen. In practice, the trial function is often a linear combination of orthogonal basis functions and depends on a number of parameters $\lambda_1, \lambda_2, \lambda_3, \ldots$, such as the coefficients used to form the linear combination of basis functions. The integral

$$E' = \frac{\int \chi(\lambda_1, \lambda_2, \lambda_3, ..)^* \hat{H} \chi(\lambda_1, \lambda_2, \lambda_3, ..) d\tau}{\int \chi(\lambda_1, \lambda_2, \lambda_3, ..)^* \chi(\lambda_1, \lambda_2, \lambda_3, ..) d\tau} \qquad (2)$$

is found and minimized to calculate the trial energy E'_{min} by adjusting the values of parameters $\lambda_1, \lambda_2, \lambda_3, \ldots$.

$$\partial E'/\partial \lambda_1 = 0 \qquad \partial E'/\partial \lambda_2 = 0 \qquad \partial E'/\partial \lambda_3 = 0 \quad \ldots$$

The resulting energy E'_{min} is an approximation (an **upper bound**) to the ground state energy E_0. And $\chi(\lambda_1, \lambda_2, \lambda_3, \ldots)$ is an approximation to the ground state wave function. By taking a sufficiently large number of λ_i parameters and basis functions of well-chosen form, very close approximations to the true energy and wave function can be obtained.

Application of Variational Theory to the Helium Atom The variational method can be used to obtain accurate values for the ground state energy of the helium atom. As an initial guess for the wave function, we can use the product of two 1s H orbitals:

$$\chi(r_1, r_2) = \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{3/2} \exp(-Z' r_1 / a_0)\, \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{3/2} \exp(-Z' r_2 / a_0) \qquad (3)$$

Each electron "sees" an **effective nuclear charge $Z' < 2$** because the other electron "screens" or "shields" it from the nucleus. Based on this consideration, we'll try using the effective nuclear charge Z' as a variational parameter.

Substituting our trial wave function $\chi(r_1,r_2)$ (equation 3) into the expression for the trial energy E' (equation 2) and integrating gives

$$E' = \left[(Z')^2 - \frac{27}{8} Z'\right] \frac{e^2}{4\pi\varepsilon_0 a_0}$$

We choose Z' to give the lowest energy by minimizing E' with respect to Z'. Setting the derivative

$$\frac{\mathrm{d}\,E'}{\mathrm{d}\,Z'} = \left(2Z' - \frac{27}{8}\right) \frac{e^2}{4\pi\varepsilon_0 a_0}$$

equal to zero, we obtain

$$Z'_{\text{min}} = 27/16 = 1.6875 \qquad E'_{\text{min}} = -1.24 \times 10^{-17}\ \text{J}$$

compared to the experimental ground state energy -1.2657×10^{-17} J. *Not too bad!* Only a 2 % error (about 150 kJ per mole)! Notice that the trial energy E'_{min} is larger than the true ground state energy of the helium atom, as required. Also, the "screened" or "effective" nuclear charge experienced by each electron is < 2, which is physically reasonable.

By using more elaborate trial wave functions $\chi(r_1,r_2)$, the ground state energy estimated by the variational method can be brought into perfect agreement with experiment.

Variational Calculations Using Linear Combinations of Functions

Variational methods are generally more useful than perturbation methods because exact solutions of related Schrödinger's equations are not required. Impressively accurate results can be obtained by using trial wave functions consisting of **linear combinations of basis sets of functions f_i,** such as

$$\chi = \sum_{i=1}^{N} c_i f_i$$

The expression for the trial energy (equation 2 above) becomes

$$E' = \frac{\int (\sum_{i=1}^{N} c_i f_i)^* \hat{H} \sum_{k=1}^{N} c_k f_k \, \mathrm{d}\tau}{\int (\sum_{i=1}^{N} c_i f_i)^* \sum_{k=1}^{N} c_k f_k \, \mathrm{d}\tau}$$

For simplicity, we will assume that the functions f_i and the coefficients c_i are real, so that $f_i^* = f_i$ and $c_i^* = c_i$. The notation can be simplified by using the abbreviations

$$H_{ik} = \int f_i \hat{H} \, f_k \, \mathrm{d}\tau$$

$$S_{ik} = \int f_i f_k \, \mathrm{d}\tau$$

to give

$$E' = \frac{\sum_{i=1}^{N} \sum_{k=1}^{N} c_i c_k H_{ik}}{\sum_{i=1}^{N} \sum_{k=1}^{N} c_i c_k S_{ik}}$$

Notice that $S_{ik} = S_{ki}$. And, less obviously, because $\hat{H}$ is Hermitian, $H_{ik} = H_{ki}$ Before differentiating E' with respect to c_1, c_2, c_3, …, it is convenient to write

$$E' \sum_{i=1}^{N} \sum_{k=1}^{N} c_i c_k S_{ik} = \sum_{i=1}^{N} \sum_{k=1}^{N} c_i c_k H_{ik}$$

Differentiating with respect to c_1, we find

$$2E'\sum_{k=1}^{N} c_k S_{1k} + \frac{\partial E'}{\partial c_1}\sum_{i=1}^{N}\sum_{k=1}^{N} c_i c_k S_{ik} = 2\sum_{k=1}^{N} c_k H_{1k}$$

Differentiating with respect to c_2 gives

$$2E'\sum_{k=1}^{N} c_k S_{2k} + \frac{\partial E'}{\partial c_2}\sum_{i=1}^{N}\sum_{k=1}^{N} c_i c_k S_{ik} = 2\sum_{k=1}^{N} c_k H_{2k}$$

and so on. Because we are *minimizing* E'

$$\partial E'/\partial c_1 = 0, \quad \partial E'/\partial c_2 = 0, \quad \partial E'/\partial c_3 = 0, \quad \ldots, \partial E'/\partial c_N = 0$$

which provides the linear system of N equations

$$\begin{aligned}
&\sum_{k=1}^{N} c_k (H_{1k} - E'S_{1k}) = 0 \\
&\sum_{k=1}^{N} c_k (H_{2k} - E'S_{2k}) = 0 \\
&\qquad\vdots \\
&\sum_{k=1}^{N} c_k (H_{Nk} - E'S_{Nk}) = 0
\end{aligned}$$

to be solved for the N unknown coefficients c_1, c_2, c_3, …, c_N.

According to linear algebra theory, there is a nontrivial solution to this system of equations (*i.e.*, not the trivial solution where $c_1 = c_2 = c_3 = \ldots = c_N = 0$) if the determinant

$$\begin{vmatrix}
H_{11} - E'S_{11} & H_{12} - E'S_{12} & \cdots & H_{1N} - E'S_{1N} \\
H_{21} - E'S_{21} & H_{22} - E'S_{22} & \cdots & H_{2N} - E'S_{2N} \\
\vdots & \vdots & & \vdots \\
H_{N1} - E'S_{N1} & H_{N2} - E'S_{N2} & \cdots & H_{NN} - E'S_{NN}
\end{vmatrix} = 0$$

equals zero. This equation is called the ***secular determinant***, an Nth order polynomial. In practice, it is solved numerically for the smallest root which corresponds to the lowest variational energy E'_{min}.

A large number of packaged computer programs are available to solve these equations.

For $N = 2$, the secular determinant reduces to

$$\begin{vmatrix} H_{11} - E'S_{11} & H_{12} - E'S_{12} \\ H_{21} - E'S_{21} & H_{22} - E'S_{22} \end{vmatrix} = 0$$

which gives the quadratic equation

$$(H_{11} - E'S_{11})(H_{22} - E'S_{22}) - (H_{21} - E'S_{21})(H_{12} - E'S_{12}) = 0$$

for the energy E'. Taking the lower root gives E'_{min}.

Orthonormal Basis Sets of Functions Considerable simplification (saving computer time) is obtained by using an orthonormal set of basis functions f_i for which

$$S_{ii} = \int f_i f_i \, \mathrm{d}\tau = 1$$

$$S_{ik} = \int f_i f_k \, \mathrm{d}\tau = 0 \qquad (i \neq k)$$

The secular determinant becomes

$$\begin{vmatrix} H_{11} - E' & H_{21} & \cdots & H_{N1} \\ H_{12} & H_{22} - E' & \cdots & H_{N2} \\ \vdots & \vdots & & \vdots \\ H_{1N} & H_{2N} & \cdots & H_{NN} - E' \end{vmatrix} = 0$$

The Helium Atom Introduces the *Pauli Exclusion Principle*

A complete wave function for an electron includes **spatial and spin factors**.

$$\psi(x, y, z, \sigma) = \psi(x, y, z)\alpha(\sigma) \quad \text{or} \quad \psi(x, y, z)\beta(\sigma)$$

A complete one-electron wave function (spatial and spin) is called a **spin orbital**. The first two spin orbitals of hydrogen-like atoms are

$$\psi_{000\frac{1}{2}} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \exp(-Zr/a_0)\,\alpha \qquad \psi_{000-\frac{1}{2}} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \exp(-Zr/a_0)\,\beta$$

From high school and first-year chemistry, we learned that no two electrons can have the same values of all four quantum numbers n, m, ℓ and m_s. This result, known as the **Pauli Exclusion Principle**, is tremendously important for chemistry! Without it, all of the electrons in atoms would collapse to the lowest energy orbitals (n = 1).

For our purposes (nonrelativistic quantum chemistry), the Pauli Exclusion Principle is treated as another postulate of quantum mechanics. Dirac's relativistic quantum mechanics – beyond the scope of this course – provides the theoretical justification for the exclusion principle.

For the ground state helium atom, electrons 1 and 2 are in the 1s level. Each of the two electrons can be spin up or spin down, so there would *appear* to be four possible spin functions:

$$\psi(1,2) = 1s(1)\alpha(1)1s(2)\alpha(2)$$

$$\psi(1,2) = 1s(1)\beta(1)1s(2)\beta(2)$$

$$\psi(1,2) = 1s(1)\alpha(1)1s(2)\beta(2)$$

$$\psi(1,2) = 1s(1)\alpha(2)1s(2)\beta(1)$$

The first two spin functions, however, cannot be used because they violate the exclusion principle. Less obviously, the last two spin functions are unacceptable too! They imply that we can distinguish electron 1 from electron 2. According to the third spin function, for example, electron 1 is in spin state +1/2 and electron 2 is in spin state – 1/2. Because individual electrons cannot be labeled, it is impossible to specify that particular electrons are in particular spin states.

Taking the linear combinations of the last two spin functions

$$\Psi_1 = \psi(1,2) + \psi(2,1) = 1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)$$

$$\Psi_2 = \psi(1,2) - \psi(2,1) = 1s(1)\alpha(1)1s(2)\beta(2) - 1s(2)\alpha(2)1s(1)\beta(1)$$

gives more reasonable results (except for a normalization factor, which has been omitted for simplicity). Ψ_1 and Ψ_2 describe states with two indistinguishable electrons. Which electron is in which orbital is not specified, nor can it be!

Spectroscopic and other experiments show, however, that only wave function Ψ_2 describes the ground state helium atom.

Notice that Ψ_2 changes sign when electron 1 and electron 2 are interchanged.

$$-\Psi_2 = \psi(2,1) - \psi(1,2)$$

For this reason, **Ψ_2 is antisymmetric under the interchange of two electrons**.

On the other hand, **Ψ_1, the wave function that is not observed, is symmetric**:

$$\Psi_1 = \psi(2,1) + \psi(1,2).$$

The generalization of the observation that the ground state of the helium atom is described by only antisymmetric wave function Ψ_2 is in accord with the more general statement of the Pauli Exclusion Principle:

All electronic wave functions must be antisymmetric under the interchange of any two electrons.

This version of the exclusion principle implies the more familiar statement that no two electrons in an atom can have all four quantum numbers that are identical.
Why? Particles with half-integral spin all require antisymmetric wave functions and are referred to as **fermions** (*e.g.*, electrons, protons, neutrons). Particles with integral spin are referred to as **bosons** and require symmetric wave functions (*e.g.*, ^{4}He nuclei).

Slater Determinants are Used to Construct Antisymmetric Wave Functions

It is fairly easy to write the antisymmetric two-electron wave function. But as the number of electrons increases, construction of antisymmetric wave functions by inspection becomes very difficult and tedious.

In 1929, Slater developed a systematic mathematical method for constructing approximate wave functions satisfying the antisymmetric requirement by writing them as **determinants**.

In a **Slater determinant**, the elements in a given column involve the same spin orbital. Elements in a given row involve the same electron.

For example, the **ground state helium wave function Ψ_2** discussed earlier is

$$\psi_2 = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}}[1s(1)\alpha(1)1s(2)\beta(2) - 1s(2)\alpha(2)1s(1)\beta(1)]$$

$\frac{1}{\sqrt{2}}$ is a normalization factor which is included to ensure that $\int \psi_2^* \psi_2 \, d\tau = 1.$

The requirement of the Pauli exclusion principle that no two electrons in an atom or molecule have all quantum numbers the same is provided for **automatically** by Slater determinants: if two rows or two columns of a determinant are identical, then the determinant is zero. Also, interchanging any two rows or any two columns changes the sign of the determinant, automatically satisfying the exclusion principle.

Next up is the **lithium atom**. In this case the Slater determinant is

$$\psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1\mathrm{s}(1)\alpha(1) & 1\mathrm{s}(1)\beta(1) & 2\mathrm{s}(1)\alpha(1) \\ 1\mathrm{s}(2)\alpha(2) & 1\mathrm{s}(2)\beta(2) & 2\mathrm{s}(2)\alpha(2) \\ 1\mathrm{s}(3)\alpha(3) & 1\mathrm{s}(3)\beta(3) & 2\mathrm{s}(3)\alpha(3) \end{vmatrix}$$

The third column could also be written with a β instead of an α. Consequently, the ground state of the lithium atom is doubly degenerate. Multiplying out a determinant with *N* rows and *N* columns gives *N*! terms, so the factor of $\frac{1}{\sqrt{3!}}$ is included as the normalization factor.

A few examples of determinants might be helpful.

For a **2 by 2 determinant**, by definition:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - cb$$

If two rows are interchanged:

$$\begin{vmatrix} c & d \\ a & b \end{vmatrix} = cb - ad = -\begin{vmatrix} a & b \\ c & d \end{vmatrix}$$

If two columns are interchanged:

$$\begin{vmatrix} b & a \\ d & c \end{vmatrix} = bc - da = -\begin{vmatrix} a & b \\ c & d \end{vmatrix}$$

If two rows are identical:

$$\begin{vmatrix} a & b \\ a & b \end{vmatrix} = ab - ab = 0$$

If two columns are identical:

$$\begin{vmatrix} a & a \\ c & c \end{vmatrix} = ac - ca = 0$$

For a **3 by 3 determinant**:

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = a\begin{vmatrix} e & f \\ h & i \end{vmatrix} - b\begin{vmatrix} d & f \\ g & i \end{vmatrix} + c\begin{vmatrix} d & e \\ g & h \end{vmatrix} = a(ei - hf) - b(di - gf) + c(dh - ge)$$

It is easy to demonstrate that the same row and column rules apply. Notice that there are a total of 3! = 6 terms for a 3 by 3 determinant.

Hartree-Fock Self-Consistent Field Method

The methods for calculating wave functions for helium and lithium illustrated so far rapidly become impractical for atoms with more electrons.

Hartree introduced the ingenious **self-consistent field (SCF) method** in 1928. It can be used to calculate wave functions for any atom with predicted energies that agree with measured values to about 1 % or better.

The SCF method is based on products of one-electron wave functions for hydrogen-like atoms. But hydrogen-like wave functions employ the full nuclear charge, *Z*. Hartree reasoned that the **outer electrons would be more strongly shielded from the nuclear charge by the inner electrons**. The outermost electrons might experience an effective nuclear charge considerably smaller than *Z*.

Hartree used a variational function φ, which is the product of *N* orbitals g_i that contain parameters, including effective nuclear charge, to be optimized by the variational method.

$$\varphi = g_1(r_1,\theta_1,\phi_1)\, g_2(r_2,\theta_2,\phi_2) \cdots g_N(r_N,\theta_N,\phi_N)$$

Each orbital in the variational function for *N* electrons is the product of radial factor $h_i(r_i)$ and a spherical harmonic $Y_{\ell imi}(\theta_i,\phi_i)$.

$$g_i = h_i(r_i)\, Y_{\ell imi}(\theta_i,\phi_i)$$

Hartree's procedure was to first estimate the form the of the g_1, g_2, … g_N orbitals by assigning appropriate values of n, ℓ, and m. The wave function of the atom is the product of these orbitals, so the Schrödinger equation for the atom can be separated into N independent equations of the form

$$\left[-\frac{\hbar^2}{2m}\nabla_i^2 + V(r_i) \right] g_i = E_i g_i$$

Where m is the mass of the electron and E_i is the energy of the orbital for electron i.

The N Schrödinger equation equations are solved by successive approximation. The potential energy function $V(r_i)$ for electron i is obtained by assuming the charge of all the other electrons is "smeared out" into a spherical charge cloud. The orbital g_1 obtained in this way for electron 1 is used to improve the potential energy function $V(r_2)$ and the orbital g_2 for the second electron, and this procedure is repeated for the all of the remaining electrons. The calculations are continued until there is no significant change in the orbitals, indicating they are "self consistent". And this was accomplished, initially, without electronic computers or calculators!

Hartree allowed for spin and the Pauli exclusion principle by placing no more than two electrons in each orbital. Spin, however, was not included explicitly. Also, the Hartree wave functions were not antisymmetric with respect to the interchange of electrons.

Fock, in 1930, improved Hartree's calculations by using Slater determinants to take linear combinations of antisymmetric products of spin orbitals. A self-consistent field calculation carried out in this way is called a **Hartree-Fock calculation**.

A set of orbitals with the same principal quantum number n is called a **shell**, and a set of orbitals with the same n and ℓ values is called a **subshell** (*e.g.*, 1s, 2s, 2p, 3s. …) As the atomic number (nuclear charge) increases, the energies of the *n*s electrons become large and negative because of increased attraction to the nucleus. The energies of the *n*p electrons are more positive because they are farther from the nucleus, on average, and more effectively shielded by the inner electrons.

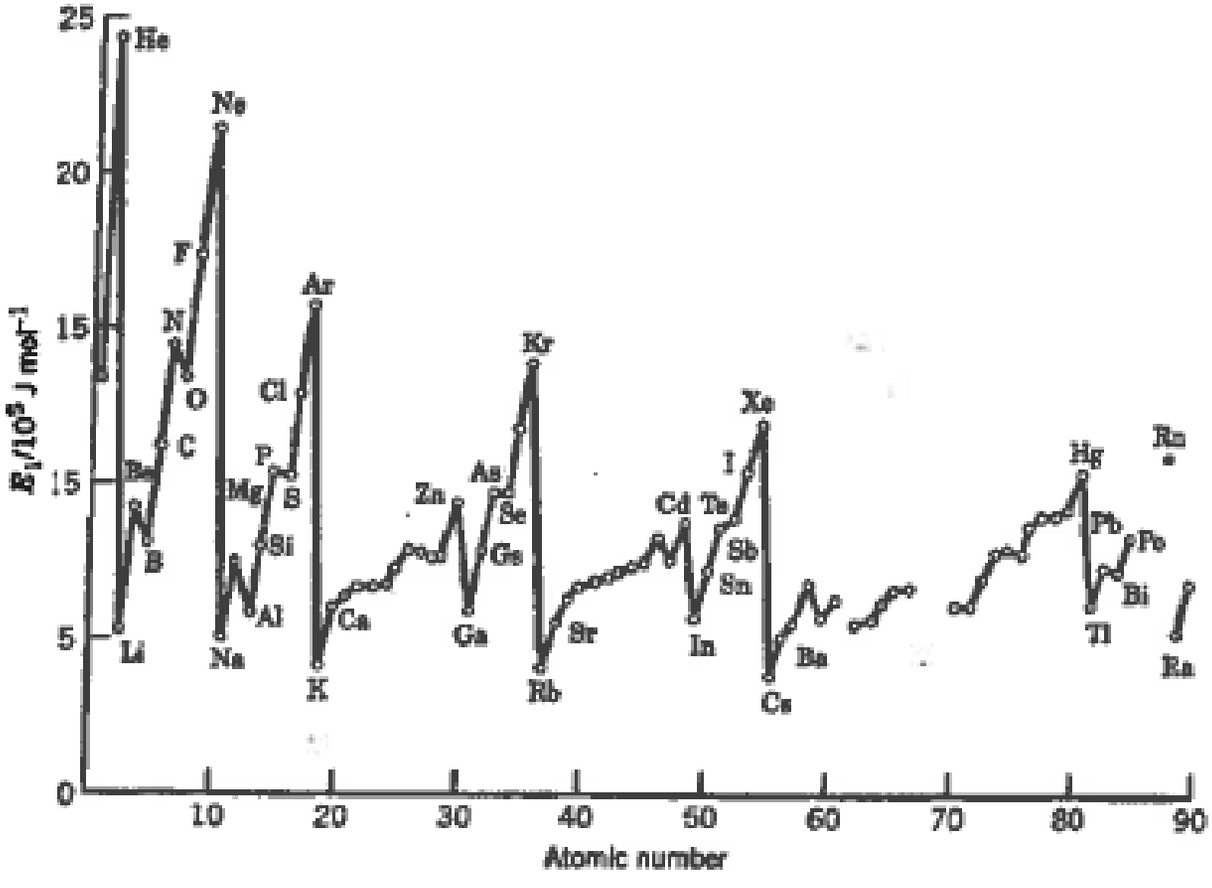
The atomic energies from Hartree-Fock SCF calculations usually agree with

experimental values to 1 % or better. The calculations allow for electron-electron interactions on an average and approximate way, by using a spherically symmetric cloud of electron charge. Instantaneous electron-electron interactions, and the resulting **correlation energy**, are not included.

A 1 % error sounds good! Unfortunately, a 1 % error in atomic energies corresponds to an error of 1 eV (about 10 kJ per mole) per atom. This is a very serious error in many chemical applications where, for example, chemical reactions and molecular conformational changes have energy differences of order of magnitude 10 kJ per mole.

Nevertheless, Hartree-Fock calculations illustrate how quantum mechanics gives us the periodic table of elements. By including more functions in the variational functions, atomic energies can be calculated with errors considerably smaller than 1 %, but at the expense of considerably greater computational effort.

Comparison of Calculated (————) and Measured (o)
Atomic Ionization Energies



The Periodic Table of Elements, Atomic Structure and the Aufbau ("Building Up") Principle

Despite ≈1 % errors in atomic energies caused the neglect of electron correlation, SCF Hartree-Fock calculations and the principles of quantum mechanics provide an explanation for the periodic table of elements which previously had been a *purely empirical construction.*

According to the Pauli exclusion principle, an s subshell can hold 2 electrons, a p subshell 6, a d subshell 10, and an f subshell 14 electrons. In general, filled subshells contain $2(2\ell+1)$ electrons. To find the **electronic configuration** of an atom in its ground state, electrons are added, filling the lower energy subshells (from SCF calculations) first, until the correct number of electrons is reached. This procedure is called the **aufbau** ("building up") **principle**.

Why is this important? Electronic configuration of the elements accounts for periodicities and trends in their chemical properties.

The Table gives the:

- electronic configuration
- term symbol (*more about this later*)
- first ionization energy
- atomic radius

for the elements, from hydrogen to krypton. The radius used here is defined as the maximum in the radial probability of the outermost orbital.

Within a row of the periodic table, the atomic radius decreases with atomic number. Within a column of the periodic table, the atomic radius increases with atomic number. These trends can be understood – quantitatively with the help of SCF calculations – in terms of two factors. First, the larger the principal quantum number, the larger the orbital. Second, increasing the effective nuclear charge decreases the size of an orbital. In a given row of the periodic table, the principal quantum number is constant, but the effective nuclear charge increases as the atomic number increases so the radius of the outermost orbital decreases. In a column of the periodic table, the effective nuclear charge remains effectively constant, but the principal quantum number increases so that the atomic radius increases.

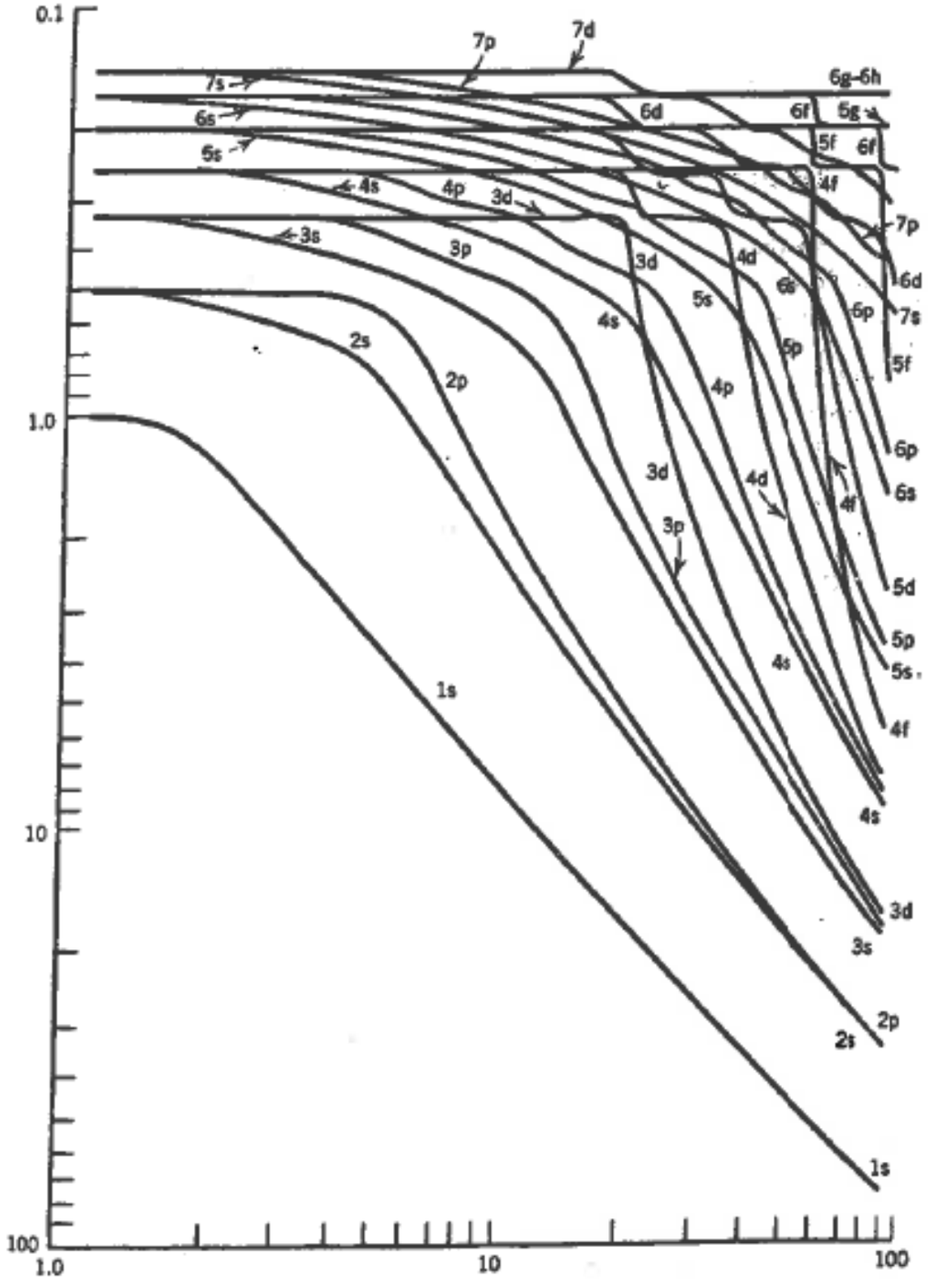
Electronic Configurations, Term Symbols, First Ionization Energies and Radius of the Outermost Orbital

Z	Atom	Configuration	Ground-State Term Symbol	First Ionization Energy, eV	Orbital Radius, pm
1	H	$1s$	$^2S_{1/2}$	13.505	52.9
2	He	$1s^2$	$^1S_0$	24.580	29.1
3	Li	[He]2s	$^2S_{1/2}$	5.390	158.6
4	Be	[He]$2s^2$	$^1S_0$	9.320	104.0
5	B	[He]$2s^22p$	$^2P_{1/2}$	8.296	77.6
6	C	[He]$2s^22p^2$	$^3P_0$	11.264	62.0
7	N	[He]$2s^22p^3$	$^4S_{3/2}$	14.54	52.1
8	O	[He]$2s^22p^4$	$^3P_2$	13.614	45.0
9	F	[He]$2s^22p^5$	$^2P_{3/2}$	17.42	39.6
10	Ne	[He]$2s^22p^6$	$^1S_0$	21.559	35.4
11	Na	[Ne]3s	$^2S_{1/2}$	5.138	171.3
12	Mg	[Ne]$3s^2$	$^1S_0$	7.644	127.9
13	Al	[Ne]$3s^23p$	$^2P_{1/2}$	5.984	131.2
14	Si	[Ne]$3s^23p^2$	$^3P_0$	8.149	106.8
15	P	[Ne]$3s^23p^3$	$^4S_{3/2}$	11.00	91.9
16	S	[Ne]$3s^23p^4$	$^3P_2$	10.357	81.0
17	Cl	[Ne]$3s^23p^5$	$^2P_{3/2}$	13.01	72.5
18	Ar	[Ne]$3s^23p^6$	$^1S_0$	15.755	65.9
19	K	[Ar]4s	$^2S_{1/2}$	4.339	216.2
20	Ca	[Ar]$4s^2$	$^1S_0$	6.111	169.0
21	Sc	[Ar]$4s^23d$	$^2D_{3/2}$	6.56	157.0
22	Ti	[Ar]$4s^23d^2$	$^3F_2$	6.83	147.7
23	V	[Ar]$4s^23d^3$	$^4F_{3/2}$	6.74	140.1
24	Cr	[Ar]$4s3d^5$	$^7S_3$	6.76	145.3
25	Mn	[Ar]$4s^23d^5$	$^6S_{5/2}$	7.432	127.8
26	Fe	[Ar]$4s^23d^6$	$^5D_4$	7.896	122.7
27	Co	[Ar]$4s^23d^7$	$^4F_{9/2}$	7.86	118.1
28	Ni	[Ar]$4s^23d^8$	$^3F_4$	7.633	113.9
29	Cu	[Ar]$4s3d^{10}$	$^2S_{1/2}$	7.723	119.1
30	Zn	[Ar]$4s^23d^{10}$	$^1S_0$	9.391	106.5
31	Ga	[Ar]$4s^23d^{10}4p$	$^2P_{1/2}$	6.00	125.4
32	Ge	[Ar]$4s^23d^{10}4p^2$	$^3P_0$	8.13	109.0
33	As	[Ar]$4s^23d^{10}4p^3$	$^4S_{3/2}$	10.00	100.1
34	Se	[Ar]$4s^23d^{10}4p^4$	$^3P_2$	9.750	91.8
35	Br	[Ar]$4s^23d^{10}4p^5$	$^2P_{3/2}$	11.84	85.1
36	Kr	[Ar]$4s^23d^{10}4p^6$	$^1S_0$	13.996	79.5

Chromium: **[Ar]$4s^13d^5$ (not [Ar]$4s^23d^4$ as might be expected)**

Copper: **[Ar]$4s^13d^{10}$ (not [Ar]$4s^23d^9$ as might be expected)**

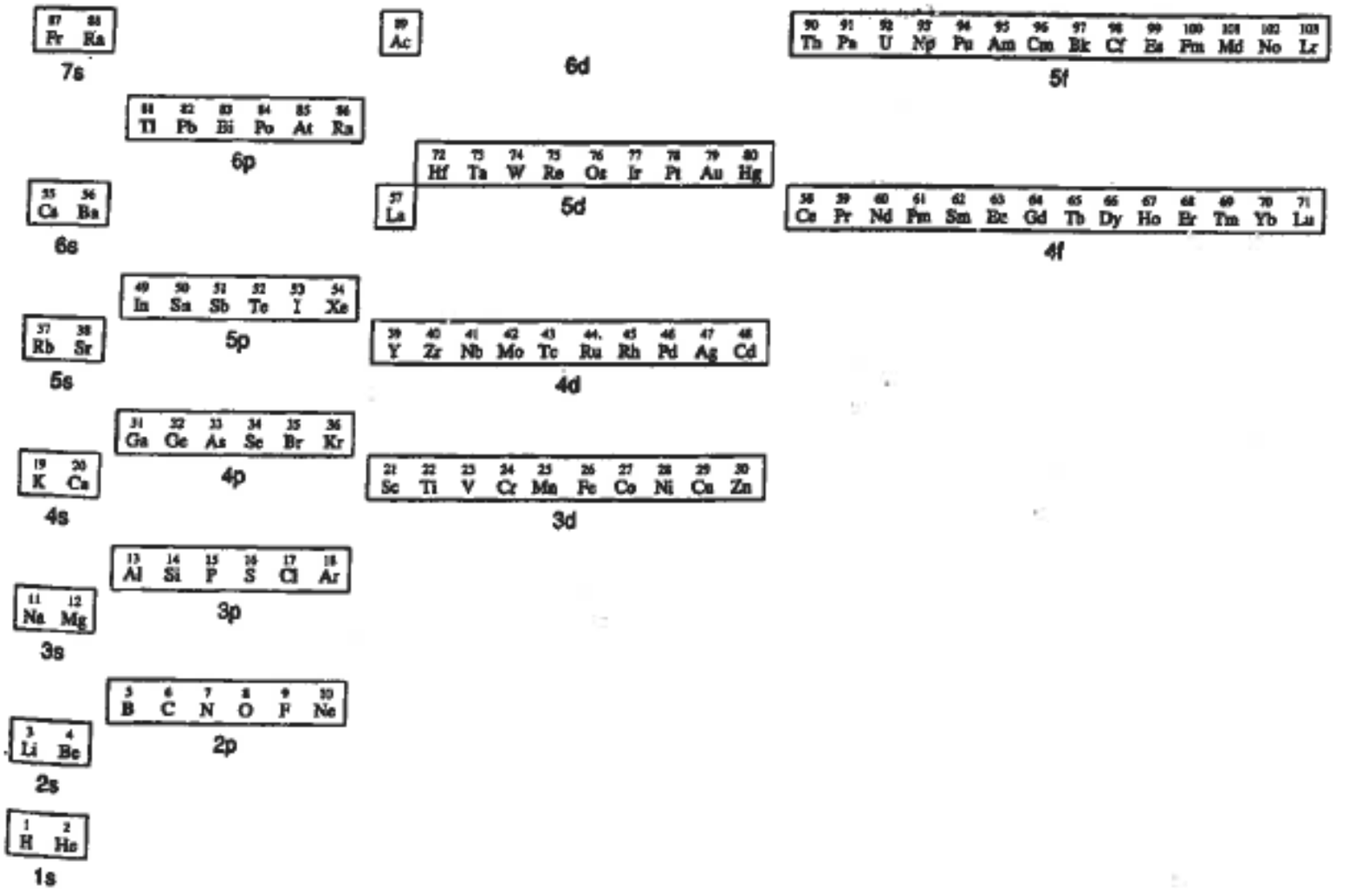
Energies of Atomic Orbitals Relative to E_1 for Ground-State Hydrogen



Notice: E_{4s} **drops below** E_{3d}

Periodic Table of the Elements

(the relative energies of the orbitals are indicated by their vertical height)



Ionization Energies

The ionization energy is the energy required to remove an electron completely from a gaseous atom, ion or molecule (in the ground state, unless noted otherwise). Ionization energies can be measured by irradiating gas-phase atoms with ultraviolet radiation, and noting the minimum photon energy required to produce ions.

The table in the notes includes the first ionization energies for atoms up to krypton.

$$A \rightarrow A^{+} + e^{-} \qquad I$$

Notice that helium is the most difficult atom to ionize, followed closely by neon. The ionization energies of the inert gases decrease with increasing atomic radius.

The alkali metals are the easiest atoms to ionize because the outermost shell is occupied by only a single electron. In the series lithium, sodium, potassium, rubidium, cesium, the ionization energy decreases because of the increasing size of the outer orbital containing the single electron.

Interestingly, the ionization of energies of the halogens are almost as large as those of the inert gases. The electrons in the outer orbitals of the halogens are all roughly the same distance from the nucleus and are shielded from the nuclear charge mainly by electrons in the inner orbitals.

It is more difficult, but definitely feasible, to measure second and subsequent ionization energies.

$$A^{+} \rightarrow A^{2+} + e^{-} \qquad II$$
$$A^{2+} \rightarrow A^{3+} + e^{-} \qquad III$$
$$A^{3+} \rightarrow A^{4+} + e^{-} \qquad IV$$

After the first electron is removed, it becomes more difficult to remove an electron, and so on. The tabulated results illustrate the especially large increase in ionization energy after all the electrons in an outer shell have been removed.

Ionization Energies for the First Six Elements in Electron Volts

Element	Ionization Energy/eV					
	I	II	III	IV	V	VI
H	13.60					
He	24.59	54.42				
Li	5.39	75.64	122.45			
Be	9.32	18.21	153.89	217.71		
B	8.30	25.15	37.93	259.37	340.22	
C	11.26	24.38	47.89	64.49	392.08	489.98

Electronic Configuration of Atoms

Hartree-Fock SCF calculations:
- ♦ hydrogen-like single-electron orbitals
- ♦ nuclear screening to allow for e-e interactions
- ♦ electron indistinguishability
- ♦ spin functions

gave the first accurate account of the periodic table of elements and physical properties such atomic ionization energies and sizes. Considering that *no empirical parameters* (*and no computers!*) were used, this was a remarkable achievement.

The order of the energies of the various subshells agrees with observations:

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s …

Notice that the energies of the 2s and 2p orbitals are not the same as they are for hydrogen-like (single-electron) atoms. The degeneracy of the 2s and 2p orbitals for hydrogen-like atoms is a consequence of the purely 1/*r* Coulombic potential energy (no nuclear screening or electron-electron interactions).

For Hartree-Fock calculations on multi-electron atoms, the potential energy depends on 1/*r and on screening of the nuclear charge*. Electrons in 2p orbitals are partially screened from the nucleus by the 2s electrons, so the 2p electrons have higher energies, in agreement with experiment. For similar reasons, 4s fills before 3d.

Notice an interesting exception to the simple filling order at chromium.

	Z = 23	**vanadium**	**[Ar]$4s^2 3d^3$**	**3 unpaired electrons**
Expect:	~~**Z = 24**~~	~~**chromium**~~	~~**[Ar]$4s^2 3d^4$**~~	~~**4 unpaired electrons**~~
Instead:	**Z = 24**	**chromium**	**[Ar]$4s^1 3d^5$**	**6 unpaired electrons**

Instead of [Ar]$4s^2 3d^4$, chromium has the configuration [Ar]$4s^1 3d^5$ because of the extra stability conferred by the **higher spin** of a half-filled s and d orbitals. (*More on this later*.) Similar exceptions occur for copper and some heavier elements.

Atomic Term Symbols

Many of the electron configurations we have used are *ambiguous*. Consider, for example, the $1s^2 2s^2 2p^2$ electron configuration of the carbon atom. The two 2p electrons could be in any of the p_x, p_y, or p_z orbitals, and still satisfy the Pauli Exclusion Principle. We will see that **electron-electron repulsion and the Pauli exclusion principle splits configurations into *terms* (states) with different energies.**

Term symbols

Orbital and spin angular momentum are used to give a more detailed and informative description of atomic states. For hydrogen-like (single-electron) atoms, n, ℓ, m and m_s are said to be **"good" quantum numbers** because the operators $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\vec{S}_z$ all commute with the Hamiltonian operator $\hat{H}$ for the total energy.

But for multi-electron atoms, the values of n, ℓ, m and m_s for the various electrons are generally **not good quantum numbers** as a result of electron-electron interactions.

What to do?

Russel-Saunders Spin-Orbit Coupling for Light ($Z < 40$) Atoms

The total angular momentum (the vector quantity $\vec{J}$) is conserved for an isolated atom, so J is always a valid quantum number.

The magnitude of $\vec{J}$ is $\left|\vec{J}\right| = \sqrt{J(J+1)}\,\hbar$.

For "light" atoms ($Z < 40$), the interaction between orbital and spin angular momentum is found to be weak, so $\vec{L}$ and $\vec{S}$ are *separately conserved*. Under these conditions, L and S are said to be "almost" good quantum numbers defined by

$$\left|\vec{L}\right| = \sqrt{L(L+1)}\,\hbar$$

$$\left|\vec{S}\right| = \sqrt{S(S+1)}\,\hbar$$

Specifying *L* and *S* provides more information about the state of an atom than specifying *J* alone. (*Notice that L and S are quantum numbers, not the magnitudes of the* $\vec{L}$ *and* $\vec{S}$ *vectors*.)

The separate determination of $\vec{L}$ and $\vec{S}$ and their coupling together to form the total angular momentum $\vec{J}$ is called **Russell-Saunders coupling** or **spin-orbit coupling**.

For an *N*-electron atom, the total orbital angular momentum and total spin angular momentum are obtained by vector addition of the contribution from each electron

$$\vec{L} = \sum_{i=1}^{N} \vec{l}_i$$

$$\vec{S} = \sum_{i=1}^{N} \vec{s}_i$$

Only electrons in unfilled subshells contribute to $\vec{L}$ and $\vec{S}$.

Recall the *x*-, *y*- and *z*-components of the angular momentum cannot be determined simultaneously, so the vector addition of the angular momenta of the electrons cannot be carried out in practice. But it is possible to determine *one* of the components of the electron angular momenta, the *z*-component by convention. The *z*-components of the orbital and spin angular momenta, defined as *M* and M_s, are the simple scalar sums

$$L_z = \sum_{i=1}^{N} l_{zi} = \sum_{i=1}^{N} m_i = M$$

$$S_z = \sum_{i=1}^{N} s_{zi} = \sum_{i=1}^{N} m_{si} = M_s$$

The Russell-Saunders scheme for light atoms involves determining the total orbital angular momentum $\vec{L}$ and the total spin angular momentum $\vec{S}$, and then adding them together to calculate the total angular momentum $\vec{J}$.

$$\vec{J} = \vec{L} + \vec{S}$$

The good quantum numbers are L, S, M, M_s and of course J.

The results are concisely represented by an **atomic term symbol** of the form

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

***L* is the total orbital angular momentum quantum number.**

***S* is the total spin quantum number**

$2S + 1$ is called the spin multiplicity

***J* is the total angular momentum quantum number.**

L has values 0, 1, 2, 3, … By analogy with the lower-case letters s, p, d, f, … for hydrogen-like atoms assigned to orbitals with angular momentum quantum numbers $\ell = 0, 1, 2, 3, \ldots$, the term symbols assigned to the total orbital angular momentum of multi-electron atoms are the upper-case letters:

L =	0	1	2	3	4	5
	S	P	D	F	G	H

The spin quantum number S has values such as 0, ½, 1, 3/2, 2, … The left superscript on a term symbol, $2S + 1$, the **spin multiplicity**, can therefore take positive integer values 1, 2, 3, 4, …

A few examples might be helpful. Recall that for a given value of n (the principal quantum number for hydrogen like atoms): $\ell = 0, 1, 2, \ldots, n-1$

$m = -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell.$

Example 1. Find the term symbol for $1s^2$ (filled 1s shell)

In this case ($\ell = 0$), there is only one possible set of values for m_1, m_{s1}, m_2, m_{s2}:

m_1	m_{s1}	m_2	m_{s2}	M	M_s
0	–1/2	0	+1/2	0	0

Because the only value of M is 0, L must be zero too ($-L \le M \le L$), so we use the letter S (*not* the spin quantum number, *not* the magnitude of $\vec{S}$, and *not* italic!) for the term symbol. Similarly, the fact that M_s is zero implies that S is zero. So the term symbol is

$$^{2S+1}S_J = {}^1S_0 \qquad \text{(“singlet S zero”)}$$

The same term symbol is obtained for the two-electron configurations $2s^2$, $3s^2$, $4s^2$, …

Example 2. Find the term symbol for np^6

An np^6 configuration also has the term symbol $^1S_0$. This is because the six electrons in the three np orbitals have the ($n_i = n$, $l_i = 1$, m_i, m_{si}) quantum numbers:

(n, 1, 1, ±1/2)
(n, 1, 0, ±1/2)
(n, 1, –1, ±1/2)

Adding the m_i values gives $M = 1 + 1 + 0 + 0 - 1 - 1 = 0$. Adding the m_{si} also gives zero, and so the correct term symbol is $^1S_0$.

Example 3. Find the term symbol for nd^{10}

The 10 electrons in the filled nd subshell have the quantum numbers:

(n_i, 2, 2, ±1/2)
(n_i, 2, 1, ±1/2)
(n_i, 2, 0, ±1/2)
(n_i, 2, –1, ±1/2)
(n_i, 2, –2, ±1/2)

useful rule:

the number of combinations of magnetic quantum numbers is $(2S+1)(2L+1) = (1)(1) = 1$.

Once again $M = 0$, $M_s = 0$, and the term symbol is $^1S_0$. These examples illustrate that ***completely filled inner subshells can be ignored when finding the term symbol for atoms with incompletely filled subshells***. For example, the term symbol for the configuration $1s^2 2s^2 2p^2$ will be identical to the term symbol for $2p^2$.

Example 4. Find the term symbol for $1s^1 2s^1$ (an excited helium atom)
All of the l_i and m_i values are 0. The possible combinations of the m_{si} values are:

m_1	m_{s1}	m_2	m_{s2}	M	M_s	M_J
0	+1/2	0	+1/2	0	1	1
0	+1/2	0	–1/2	0	0	0
0	–1/2	0	+1/2	0	0	0
0	–1/2	0	–1/2	0	–1	–1

There are four possibilities because there are two possible spins for the electron in the 1s orbital and for each of these possibilities there are two possible spins for the electron in the 2s orbital.

All of the M values are zero, so they must all correspond to $L = 0$.

The largest value of M_s is 1. Therefore, $S = 1$ (Why? Because $-S \leq M_s \leq S$.) and the M_s values –1, 0, +1 correspond to $\boldsymbol{L = 0, S = 1}$ **with** $\boldsymbol{J = 1}$ (with $-1 \leq M_J \leq 1$).

After eliminating these three entries from the total of four, the remaining $M = 0$, $M_s = 0$ entry corresponds to a second pair of L, S values: $\boldsymbol{L = 0}$ **and** $\boldsymbol{S = 0}$ **with** $\boldsymbol{J = 0}$.

The two $^{2S+1}L_J$ term symbols for $1s^1 2s^1$ consistent with these results are

$^3S_1$ (called a "**triplet S**" state) $^1S_0$ (called "**singlet S**" state)

Why is this important? These two term symbols correspond to electronic states with **different energies**. The triplet $^3S_1$ state the two electrons have parallel spins. In the singlet $^1S_0$ the electrons have opposite spins. We can show that ***the energy of the triplet state is lower***. The calculations are a bit long. Only the results are quoted here.

Energy of the $^1S_0$ Singlet and Triplet $^3S_0$ State for $1s^12s^1$ *(Details in Tutorial #2!)*

$$E_{\text{singlet}} = E_{1s} + E_{2s} + J_{12} + K_{12}$$

$$E_{\text{triplet}} = E_{1s} + E_{2s} + J_{12} - K_{12}$$

J_{12} is the **Coulomb integral** giving the electron-electron repulsion energy (positive) between an electron in the 1s orbital and an electron in the 2s orbital:

$$J_{12} = \frac{e^2}{4\pi\varepsilon_0}\iint[1\text{s}(1)]^2\frac{1}{r_{12}}[2\text{s}(2)]^2\,\text{d}\tau_1\,\text{d}\tau_2$$

K_{12} is called the **exchange integral** (also positive) because the electrons have been interchanged in the integration. *They are in two different orbitals at the same time!* Notice that K_{12} decides the energy difference between the singlet and triplet states:

$$K_{12} = \frac{e^2}{4\pi\varepsilon_0}\iint[1\text{s}(1)2\text{s}(2)]\frac{1}{r_{12}}[1\text{s}(2)2\text{s}(1)]\text{d}\tau_1\,\text{d}\tau_2$$

The exchange integral is positive, so the *energy of the triplet state is lower* than the energy of the singlet state by $2K_{12}$.

Why? Unlike the Coulomb integral J_{12} for electron-electron repulsion, the exchange integral K_{12} responsible for the lower energy of the triplet state has ***no classical physical interpretation***. K_{12} includes the repulsion energy between each electron and *itself*, in different orbitals! K_{12} results from Pauli's exclusion principle that requires antisymmetric wave functions. On average, the electrons are closer to the nucleus in the triplet state. Although spin is not contained in the Hamiltonian total energy operator, spin, indirectly, influences the energy. In general, atomic states with higher spin have lower energy. From electronic spectroscopy, for example, the triplet $1s^12s^1$ excited state of the helium atom is 0.7961 eV lower than that of the singlet state.

Example 5. Find the term symbol for $1s^2 2s^2 2p^2$ (the carbon atom)

At first glance, it is a complicated problem to count the number of n_i, l_i, m_i, m_{si} combinations for six electrons in two different shells and a partially filled subshell. But as shown earlier, we can ignore the filled 1s and 2s shells (contribution zero orbital and spin angular momentum).

So the problem reduces to counting the number of arrangements for

$$[\text{Be}]2p^2 \quad = \quad 2p^2$$

Though simplified, the problem is still not trivial. We must assign two electrons to two of six possible spin orbitals. There are 6 choices for the first electron and 5 remaining choices for the second electron, for a total of 30 possibilities!

But wait! Electron 1 cannot be distinguished from electron 2. In other words, the "first" and "second" electron terminology is physically meaningless. Swapping electrons 1 and 2 in each of the 30 arrangements cannot produce a second new arrangement. Consequently, the 30 possibilities for distinguishable electrons are reduced to 15 possible arrangements for *indistinguishable* electrons.

In general, the number of distinct ways to assign N electrons to G spin orbitals belonging to the **same subshell** is

$$\frac{G!}{N!(G-N)!}$$

$N = 2$ and $G = 6$ for the $2p^2$ electrons gives $6!/(2!4!) = 15$ arrangements to consider.

Other useful rules: $-L \leq M \leq L$ $\qquad$ $-S \leq M_s \leq S$

$$M = \sum_{i=1}^{N} m_i \qquad M_s = \sum_{i=1}^{N} m_{si}$$

The 15 possible sets of m_1, m_{s1}, m_2, m_{s2} values for the $2p^2$ configuration are:

no.	m_1	m_{s1}	m_2	m_{s2}	M	M_s	M_J	
~~1.~~	~~+1~~	~~+1/2~~	~~+1~~	~~+1/2~~	~~+2~~	~~+1~~	~~+3~~ *	
1.	+1	+1/2	+1	–1/2	+2	0	+2	^{1}D
~~2.~~	~~+1~~	~~+1/2~~	~~+1~~	~~+1/2~~	~~+2~~	~~0~~	~~+2~~**	
2.	+1	+1/2	0	+1/2	+1	+1	+2	^{3}P
3.	+1	+1/2	0	–1/2	+1	0	+1	^{1}D
4.	+1	+1/2	–1	+1/2	0	+1	+1	^{3}P
5.	+1	+1/2	–1	–1/2	0	0	0	^{1}D
6.	+1	–1/2	0	+1/2	+1	0	+1	^{3}P
7.	+1	–1/2	0	–1/2	+1	–1	0	^{3}P
8.	+1	–1/2	–1	+1/2	0	0	0	^{3}P
9.	+1	–1/2	–1	–1/2	0	–1	–1	^{3}P
10.	0	+1/2	0	–1/2	0	0	0	^{1}S
11.	0	+1/2	–1	+1/2	–1	+1	0	^{3}P
12.	0	+1/2	–1	–1/2	–1	0	–1	^{1}D
13.	0	–1/2	–1	+1/2	–1	0	–1	^{3}P
14.	0	–1/2	–1	–1/2	–1	– 1	–2	^{3}P
15.	–1	+1/2	–1	–1/2	–2	0	–2	^{1}D

*Entries with $m_1 = m_2$ and $m_{s1} = m_{s2}$ are not allowed! (*Why?*)
**Entries obtained by simply interchanging electrons 1 and 2 are not included! (*Why?*)

Now we must deduce the possible L and S values. The largest value of M is 2, and this value occurs only for $M_s = 0$. So there must be a ^{1}D state with $L = 2$ and $S = 0$. The ^{1}D state accounts for the five table entries numbered 1, 3, 5, 12 and 15 with M values 2, 1, 0, 1, –1, –2. There are 10 remaining entries.

Notice that the number of sets of magnetic and spin quantum numbers with given L and S values is (2L + 1)(2S + 1)

The largest remaining value of M is 1, implying $L = 1$ with $M = 1, 0, –1$. Each of these values of M occurs with $M_s = 1$, 0, or –1. Therefore, we have a state with $L = 1$ and $S = 1$ designated by ^{3}P.

Eliminating the five ^{1}D and nine ^{3}P entries leaves only one entry (number 10) with M = 0 and M_s = 0. This must be a ^{1}S state.

To complete the term symbols, we need to specify the possible J values for the ^{1}D, ^{3}P, and ^{1}S states. The entries for the ^{1}D (L = 2, S = 0) state have M_J values of 2, 1, 0, –1, –2, corresponding to J = 2, so the complete term symbol is $^1D_2$.

The 9 entries for the ^{3}P state have the M_J values 2, 1, 1, 0, 0, –1, 0, –1, –2. We have one set of M_J values with 2, 1, 0, –1, –2 corresponding to J = 2. The other sets of M_J values are 1, 0, –1, corresponding to J = 1, and finally M_J = 0 corresponding to J = 0. The J values for the ^{3}P states are therefore 2, 1, and 0 and the complete term symbols are $^3P_2$, $^3P_1$, and $^3P_0$.

The ^{1}S state can only have J = 0, so the completed term symbol is $^1S_0$.

In summary, we can say that the term symbols for the carbon atom with the $1s^2 2s^2 2p^2$ configuration (and for other atoms with the [filled]np^2 configuration):

$$^1D_2 \quad ^3P_2 \quad ^3P_1 \quad ^3P_0 \quad ^1S_0$$

The values of J for each completed term symbol can be determined from the L and S values. Recall the vector definition of the total atomic angular momentum:

$$\vec{J} = \vec{L} + \vec{S}$$

The largest value that J can have is in the case where both $\vec{L}$ and $\vec{S}$ are pointing in the same direction, where $J = L + S$. The smallest value J we can have is when $\vec{L}$ and $\vec{S}$ point in the opposite direction where $J = |L - S|$. For given L and S values, the values of J are

$$J = L + S, L + S - 1, L + S - 2, \ldots, |L - S|$$

Applying this relation to the ^{3}P term we deduced for the np^2 configuration with L = 1 and S = 1 gives J = 1 + 1, 1 + 1 – 1, 1 – 1, which agrees with J = 2, 1, 0 derived above.

Hund's Rules Decide the Ground Electronic State

Each of the atomic states designated by the term symbol for an electronic configuration has a certain energy. This energy can be calculated by solving Schrödinger's equation (numerically for multi-electron atoms). In practice, it is much easier to use the three empirical rules developed by the spectroscopist Frederick Hund.

1. The state with the **largest *S*** (and therefore largest multiplicity $2S + 1$) value is the most stable state. Stability decreases with decreasing *S*.

2. For states with **same *S* value**, the state with the **largest value of *L*** is the most stable.

3. **a)** For states with same value of *S* and *L* for a subshell that is less than half filled, the state with the smallest *J* value is most stable.

b) For states with same value of *S* and *L* for a subshell that is more than half filled, the state with the largest *J* value is most stable.

Example 1. Find the ground state for the $1s^1 2s^1$ configuration

For the $1s^1 2s^1$ configuration, we derived the term symbols

$^3S_1$ (triplet S state) $^1S_0$ (singlet S state)

According to Hund's rules, the triplet state (larger value of *S*) is the lower-energy ground state, in agreement with theory and experiment.

Example 2. Find the ground state for the boron atom with configuration [Be]$2p^1$

In this case $L = 1$, $S = ½$, and $J = 1/2$ or $3/2$, so there are two term symbols

$^2P_{3/2}$ $^2P_{1/2}$ The p shell is less than half filled. Hund's rule 3a) gives $^2P_{1/2}$ for the ground state.

Example 3. **Find the ground state for the carbon and related np^2 configurations**

For the np^2 configuration, we derived the term symbols

$$^1D_2 \qquad ^3P_2 \qquad ^3P_1 \qquad ^3P_0 \qquad ^1S_0$$

According to Hund's rules, the triplet $^3P_2$, $^3P_1$,$^3P_0$ states have lower energies than the singlet $^1D_2$ and $^1S_0$ states. Within the triplet states (identical *L* and *S* values, shell less than half filled), the $^3P_0$ state with the smallest *J* value is most stable.

! *Warning* !

Of the various kinds of atomic angular momentum (*e.g.*, orbital and spin), only the total angular momentum $\vec{J}$ is strictly conserved. The Russell-Saunders scheme breaks down for heavy atoms ($Z > 40$) because of the increased strength of the interaction between orbital and spin angular momentum. For heavy atoms, the Russell-Saunders spin-orbit scheme is replace by a *J*-*J* coupling scheme (not covered here).

The total angular momentum is important because states with different angular momentum have different energies.

Why? Because electrons repel each other electrostatically, and the strengths of the repulsions depend on the distribution of electron density, which in turn is directly related to the shape of the orbitals given by ℓ_i and m_i. This is called orbit-orbit or ($\ell\ell$) interaction. In addition, atomic orbitals must obey Pauli's Exclusion Principle. It dictates the possible combinations of orbital and spin states, producing indirectly spin-spin (*ss*) and spin-orbit (ℓs) interactions.

The detailed analysis of orbit-orbit, spin-orbit, and spin-spin interactions, especially for heavy atoms, is very complicated. In general the orbital and spin angular momentum are not separately conserved. But for light atoms ($Z < 40$), like the ones we have been considering, spin-orbit interactions are relatively weak. As a result, the total orbital angular momentum and the total spin angular momentum are separately conserved (with very few exceptions).

What can atomic term symbols be used for?

Application to Spectra of Hydrogen-Like Atoms

Spectroscopic measurements give extraordinarily precise values of the energy differences between atomic states. Less obviously, valuable information about the quantum numbers of the states is also provided.

The energy levels of the quantum states of hydrogen atoms and hydrogen-like atoms are well known. But the vast majority of transitions between these states are never observed. Why?

To understand this result, it is important to recognize that photons have intrinsic angular momentum. For left-circularly polarized radiation, $m = 1$, and for right-circularly polarized photon, $m = -1$. When a photon is absorbed by a hydrogen atom or hydrogen-like atom, the angular momentum of the photon is transferred to the electron of the atom. Because angular momentum is conserved, we have the **selection rule**

$$\Delta \ell = \pm 1$$

Not surprisingly, the most intense transitions are **electric dipole transitions** involving the interaction of the electric field of the radiation with an instantaneous electric dipole of the atom. Magnetic dipole transitions are about 100,000 times weaker (less probable).

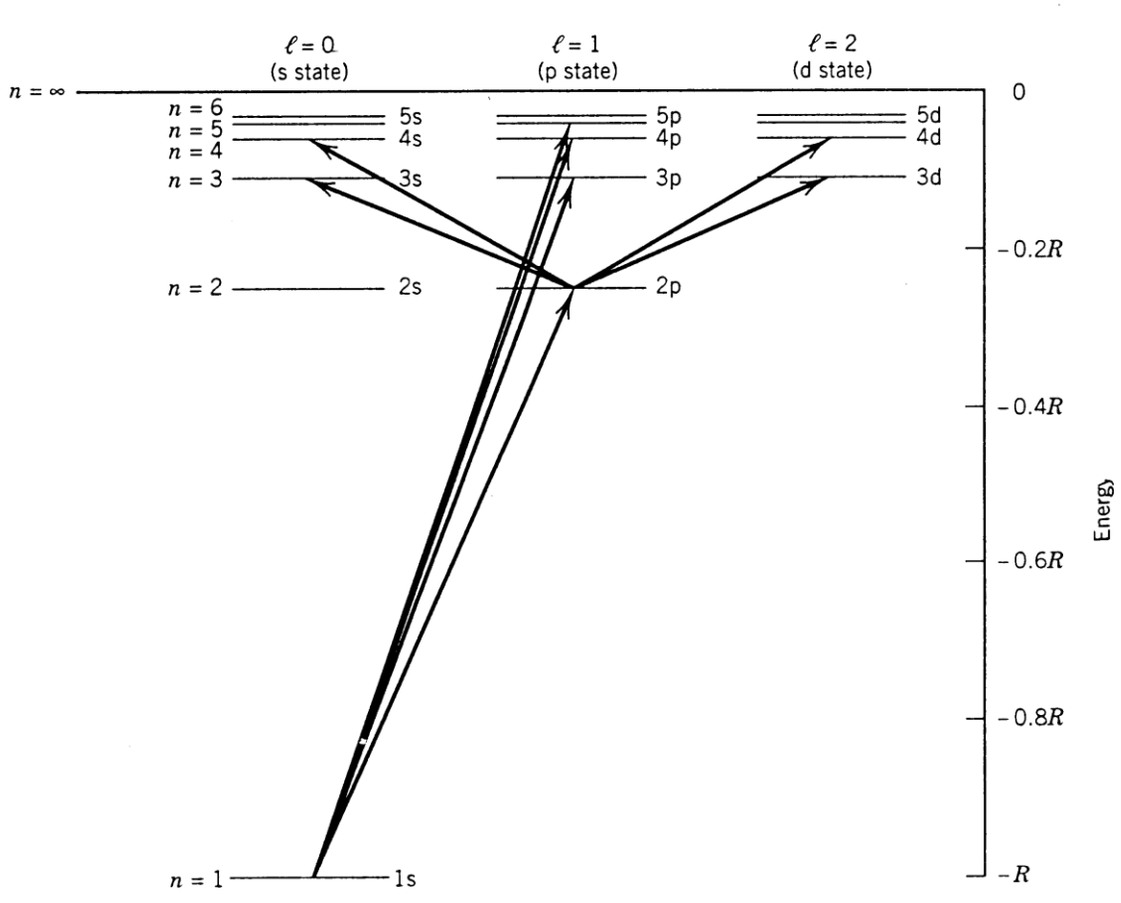
The complete selection rules for the electronic spectroscopy of hydrogen atoms and hydrogen-like atoms are:

Δn	no restrictions	$\Delta \ell = \pm 1$	$\Delta m = \pm 1$

These rules are illustrated by energy-level diagrams (called **Grotrian Diagrams** by spectroscopists, named after Dr. Grotrian, a spectroscopist) for observed transitions between different atomic states.

Grotrian Diagram for Hydrogen Atoms

(energy in units of Rydbergs)



Notice:

Allowed Transitions: p → s, s → p, d → p, p→ d, …

Forbidden Transitions: s → s, p → p, d → d, or s → d, d → s, …

Atomic Terms Symbols Are Used to Describe Atomic Spectra

The electronic spectra of multi-electron atoms are much richer in detail, as you might expect. For light ($Z < 40$) atoms, where Russell-Saunders coupling applies, the following selection rules have been verified theoretically (using time-dependent wave equations) and experimentally.

$\Delta L = \pm 1$

$\Delta S = 0$ *Why?*

The $\Delta S = 0$ rule results from the fact that the electric field associated with *electromagnetic radiation has no effect on spin angular momentum*.

In practice, the $\Delta S = 0$ rule is important chemically because it restricts transitions between singlet and triplet states.

This selection rule leads to the formation of **metastable states**.

An excited triplet state, for example, cannot emit a photon and make a transition to decay to a ground singlet state. For this reason, the lifetimes of triplet states can be unusually long and are often called “metastable”.

In practice, excited triplet states can however be converted to singlet states by collisions with other atoms or molecules, or with the walls of containers.

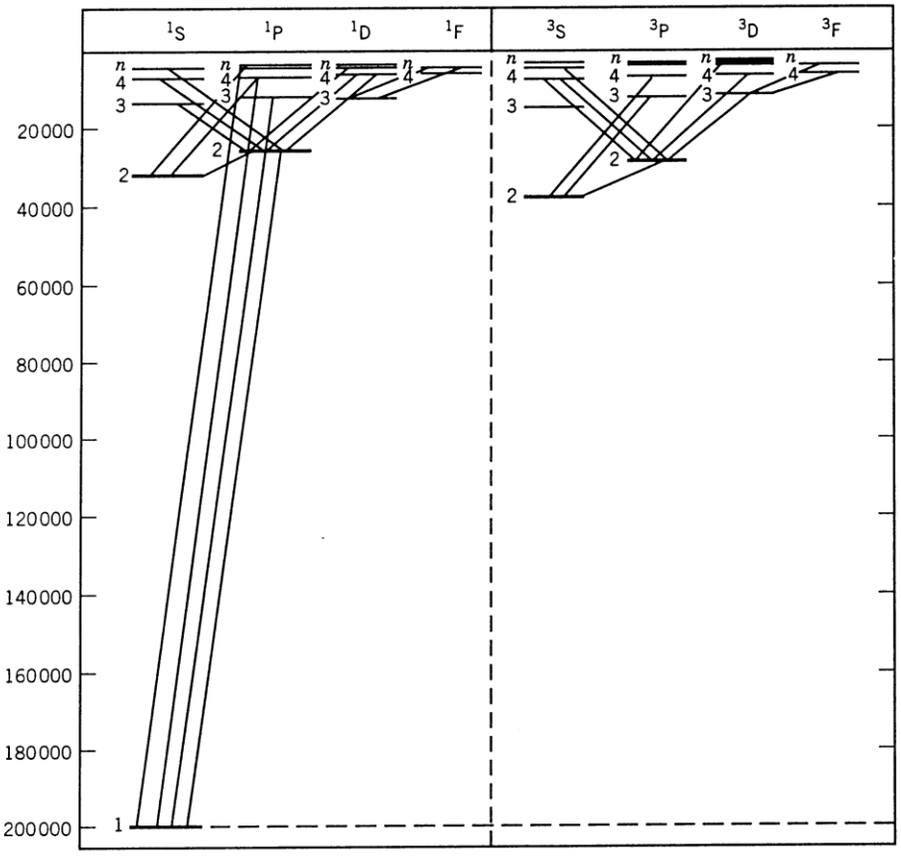
Metastable states play important roles in photochemistry and in chemical kinetics.

The importance of singlet and triplet states is nicely illustrated by the Grotrian Diagram for the helium atom.

Notice that the lowest-energy triplet state cannot make an allowed transition to the singlet ground state, which gives metastable triplet helium. For many years, it was thought that two different kinds of helium existed: orthohelium and parahelium!

Electronic Transitions for Helium Atoms

(energy in wavenumbers)



! Warning ! "Forbidden" atomic transitions can and do occur. So-called forbidden transitions, however, are usually very weak. They occur not because quantum mechanics is wrong, but as a result of approximations made in our analysis.