

Quantum Chemistry

Lecture 3

Atomic structure

NC State University

The effective potential: result of the solution of the angular part

- The solutions for the angular part results in a term in potential energy equal to:

$$V' = -\frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2}$$

- This term contains the contributions to the energy from angular terms.
- Together with the Coulomb potential the effective potential energy is:

$$V_{eff} = -\frac{Ze^2}{4\pi\epsilon_0 r} - \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2}$$

The radial equation for hydrogen

Making the above approximations we have an radial hamiltonian (energy operator)

$$\frac{\hbar^2}{2\mu} \nabla^2 R - \frac{Ze^2}{4\pi\epsilon_0 r} R - \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} R = ER$$

The solutions have the form: $R_{n,l} = N_{n,l} \rho^l e^{-\rho/2} L_{n,l}(r)$

where $\rho = 2Zr/na_0$ and $a_0 = 4\pi\epsilon_0 \hbar^2 / me^2$

$N_{n,l}$ is the normalization constant.

$L_{n,l}(r)$ is an associated Laguerre polynomial.

The Bohr Radius

The constant a_0 helps to express the radial equations in a compact form. This constant is known as the Bohr radius.

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

The Bohr radius is equivalent to 0.52977 \AA . It is named after Niels Bohr because of his contribution in creating the planetary model of the hydrogen atom (semi-classical theory). While this theory does obtain the correct energies for the hydrogen atom it fails to fully explain angular momentum and it does not explain multi-electron atoms.

Solutions of the radial equation

The normalization constant depends on n and ℓ

$$N_{n,\ell} = \left\{ \frac{(n - \ell - 1)!}{2n(n + 1)!^3} \right\} \left(\frac{n}{2a_0} \right)^{\ell+3/2}$$

The associated Laguerre polynomials are:

$$n = 1, \ell = 0, L_1^1(x) = -1$$

$$n = 2, \ell = 0, L_2^1(x) = -2! (2 - x)$$

$$n = 2, \ell = 1, L_3^3(x) = -3!$$

$$n = 3, \ell = 0, L_3^1(x) = -3! (3 - 3x + 1/2x^2)$$

$$n = 3, \ell = 1, L_4^3(x) = -4! (4 - x)$$

$$n = 3, \ell = 2, L_5^5(x) = -5!$$

Normalization of the radial functions

Each of the radial equation solutions is a polynomial multiplying an exponential. The normalization is obtained from the integral:

$$\int_0^{\infty} R_{n\ell}^* R_{n\ell} r^2 dr = 1$$

The volume element here is $r^2 dr$ which is the “r” part of the spherical coordinate volume element $r^2 \sin\theta dr d\theta d\phi$.

MAPLE worksheet

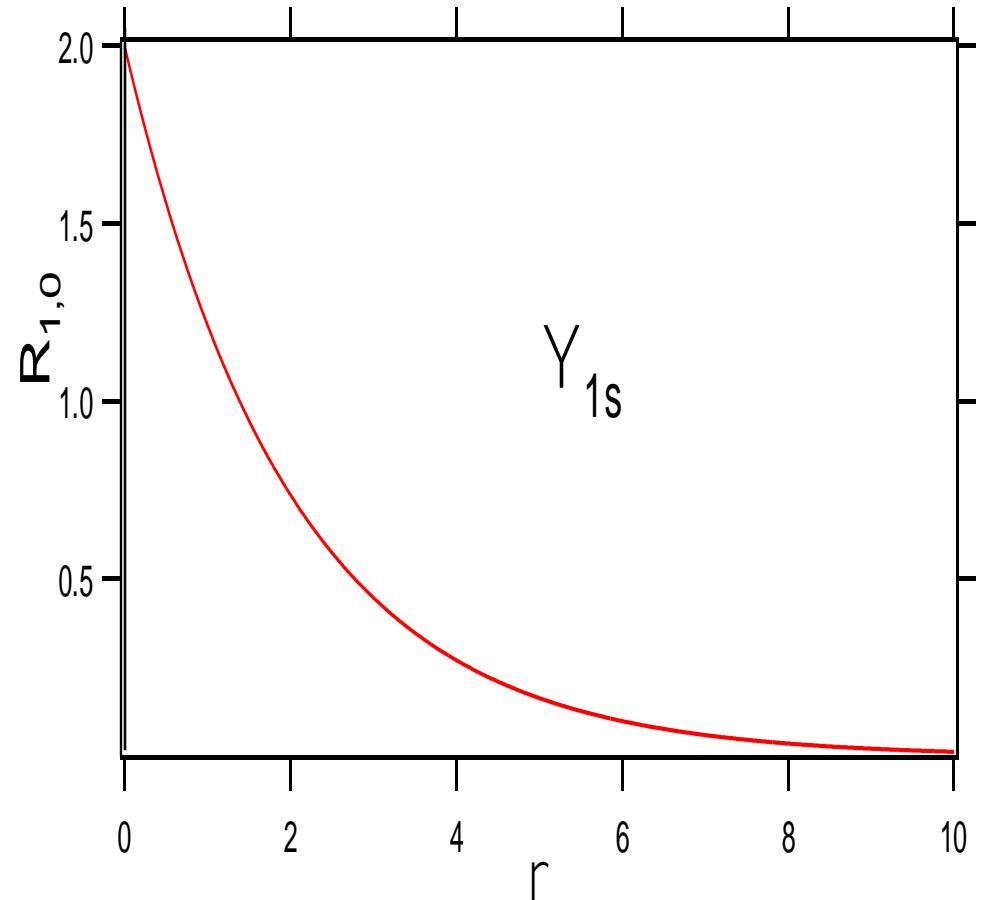
Normalization of the radial functions

A MAPLE worksheet attached to this lecture illustrates the normalization of the first three radial functions. The worksheet includes plots of the functions.

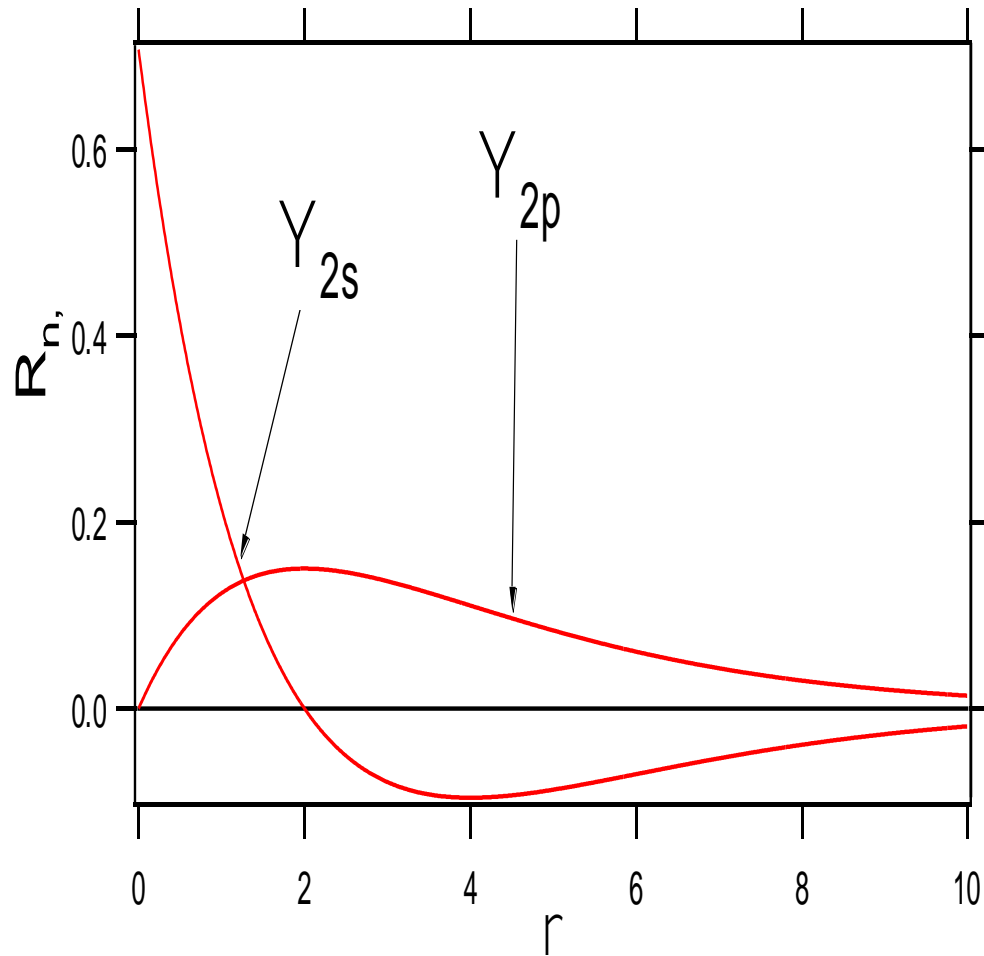
When examining a plot keep in mind that you can plot the wave function or the square of the wave function. We often plot the square of the wave function, because the integral of the square of the wave function gives the probability.

Hydrogen 1 s radial wavefunction

- The 1s orbital has no nodes and decays exponentially.
- $R_{1s} = 2(1/a_0)^{3/2}e^{-\rho/2}$
- For $n = 1$, $\rho = r/a_0$
- $n = 1$ and $\ell = 0$ are the quantum numbers for this orbital.



The Radial Distribution in Hydrogen 2s and 2p orbitals



Radial wave functions for H

$$R_{1s} = 2 \left(\frac{Z}{a} \right)^{3/2} e^{-Zr/a}$$

$$R_{2s} = \frac{1}{\sqrt{2}} \left(\frac{Z}{a} \right)^{3/2} \left(1 - \frac{Zr}{2a} \right) e^{-Zr/2a}$$

$$R_{2p} = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a}$$

$$R_{3s} = \frac{2}{3\sqrt{3}} \left(\frac{Z}{a} \right)^{3/2} \left(1 - \frac{2Zr}{3a} + \frac{2Z^2 r^2}{27a^2} \right) e^{-Zr/3a}$$

The Quantized Energy Levels

- The energy levels calculated using the Schrödinger equation are given by

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2} \frac{1}{n^2} = -\frac{R}{n^2}$$

- In units of Bohrs the Rydberg constant is

$$R = \frac{me^4}{8\varepsilon_0^2 h^2} = \frac{e^2}{(4\pi\varepsilon_0)2a_0}$$

The Rydberg Constant

- The energy levels calculated using the Schrödinger equation permit calculation of the Rydberg constant.
- One major issue is units. Spectroscopists often use units of wavenumber or cm^{-1} . At first this seems odd, but $h\nu = hc/\lambda = hc\tilde{\nu}$ where $\tilde{\nu}$ is the value of the transition in wavenumbers.

$$\tilde{R} = \frac{1}{hc} \frac{me^4}{8\varepsilon_0^2 h^2} \quad \text{in cm}^{-1}$$

The simple form for H energy levels

Using the Rydberg constant the energy of the hydrogen atom can be written as:

$$E_n = -\frac{\tilde{R}}{n^2}$$

where $R = 109,690 \text{ cm}^{-1}$

In units of eV $R = 13.6 \text{ eV}$.

Shells and subshells

- All of the orbitals of a given value of n for a shell.
- $n = 1, 2, 3, 4 \dots$ correspond to shells K, L, M, N...
- Orbitals with the same value of n and different values of ℓ form subshells.
- $\ell = 0, 1, 2, \dots$ correspond to subshells s, p, d ...
- Using the quantum numbers that emerge from solution of the Schrödinger equation the subshells can be described as orbitals.

Spectroscopy of atomic hydrogen

- Spectra reported in wavenumbers, cm^{-1}
- Rydberg fit all of the series of hydrogen spectra with a single equation, $\tilde{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$
- Absorption or emission of a photon of frequency ν occurs in resonance with an energy change, $\Delta E = h\nu$ (Bohr frequency condition).
- Solutions of Schrödinger equation result in further selection rules.

Spectroscopic transitions

- A transition requires a transfer from one state with its quantum numbers (n_1, ℓ_1, m_1) to another state (n_2, ℓ_2, m_2) .
- Not all transitions are possible: there are selection rules, $\Delta\ell = \pm 1, m = 0, \pm 1$
- These rules demand conservation of angular momentum. Since a photon carries an intrinsic angular momentum of 1.

Expectation values

The expectation (or average) value of an observable $\langle r \rangle$ is given by the general formula.

$$\langle r \rangle = \iiint_0^\infty \Psi^* r \Psi d\tau$$

As written the above integral describes the expectation value of the mean value of the radius, r . Integration over the angular part gives 1 because the spherical harmonics are normalized. The volume element can be written $d\tau = r^2 dr$. The mean value is:

$$\langle r \rangle = \int_0^\infty \Psi^* r \Psi r^2 dr = \int_0^\infty \Psi^* \Psi r^3 dr$$

Example: Average H Radius

Assuming $Z = 1$ and units of Bohrs ($a_0 = 1$), the radial normalized 1s wave function is:

$$R_{1s} = 2e^{-r}$$

The expectation value or average radius of the electron is given by

$$\langle r \rangle = \int_0^{\infty} R_{1s} r R_{1s} r^2 dr$$

Substituting in the 1s wave function we find

$$\langle r \rangle = 4 \int_0^{\infty} e^{-2r} r^3 dr$$

Example: Average H Radius

The integral can be solved to yield

$$\langle r \rangle = \left[-\frac{1}{2} (3 + 6r + 6r^2 + 4r^3) e^{-2r} \right]_0^{\infty}$$

which gives the average distance in units of Bohrs

$$\langle r \rangle = \frac{3}{2}$$

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Thus, the average distance of an electron from the nucleus is $3/2a_0$ or 0.795 Angstroms.

MAPLE worksheet on Expectation (Average) values

There is a MAPLE worksheet attached to this lecture that illustrates the use of expectation values. The example of the position $\langle r \rangle$ is given for the 1s, 2s and 3s radial wave functions. The expectation value or average value of r gives the average distance of an electron from the nucleus in a particular orbital. Since the 2s orbital has one radial node and the 3s orbital has two radial nodes the average distance of the electron from the nucleus is shown to increase as:

$$\langle r \rangle \text{ for } 3s > \langle r \rangle \text{ for } 2s > \langle r \rangle \text{ for } 1s$$

The average energy

The expectation (or average) value of the energy $\langle E \rangle$ is given by the general formula.

$$\langle E \rangle = \iiint_0^\infty \Psi^* H \Psi d\tau$$

since the hamiltonian H is the energy operator. If the wave function is not normalized this is often written as:

$$\langle E \rangle = \frac{\int_0^\infty \Psi^* H \Psi d\tau}{\int_0^\infty \Psi^* \Psi d\tau}$$

The definition of an isosurface

A second way to view the hydrogen atom can be expressed by the question, "how big is the hydrogen atom?". We can define the size of the atom in terms of an isosurface. The isosurface is defined for a given probability. For example, we can calculate how large a sphere corresponds to a 90% probability for finding the electron. This 90% isosurface defines the radius of the atom. Assuming $Z = 1$ and units of Bohrs ($a_0 = 1$) the normalized radial 1s wave function is

$$R_{1s} = 2e^{-r}$$

The density contained within a 90% probability surface will have a radius A given by

$$\int_0^A R_{1s} R_{1s} r^2 dr = 0.9$$

The 90% isosurface of the H atom

Substituting in the 1s wave function we find

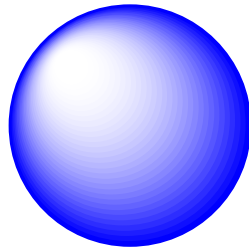
$$4 \int_0^A e^{-2r} r^2 dr = 0.9$$

This integral is readily solved to give the equation,

$$1 - (1 + 2A + 2A^2)e^{-2A} = 0.9$$

While this equation does not have analytic solution, it can readily be solved numerically to yield

$A = 2.66$. Thus, the 90% isosurface is defined as total density within 2.66 Bohrs of the nucleus.



Spin and the Pauli Exclusion Principle

The solutions to the Schrodinger equation explain the one Electron atom adequately. However, in order to move beyond a one electron atom we must introduce the concept of electron spin. The word spin arises from the fact that an electron has an apparent magnetic moment. It acts like a spinning charge. Because of the property of spin electrons populate the orbitals in pairs.

The rigorous statement of this idea is that the total wave function must be anti-symmetric with respect to electron exchange. Electrons are a member of the class of particles known as fermions. They have a half integer spin ($s = \frac{1}{2}$). No two fermions may occupy the same energy state.

Spin and Spatial Wavefunctions

We focus on He and the two-electron situation since that is both the first and simplest case where electron spin must be included. The wave function for the two electrons can be written as,

$$\Psi_{\text{total}} = \Psi_{\text{spatial}} \Psi_{\text{spin}}$$

We have already considered how the spatial wave function can arise from a product of hydrogen-like wave functions for each electron (Hartree approximation). The spin part of the wave function consists of single electron wave functions that we will call a and b , for spin-up and spin-down, respectively. The wave function must be antisymmetric with respect to electron exchange. Since there are two parts to the wave function, the antisymmetry can arise either from the spin part or the spatial part.

Symmetric and anti-symmetric wavefunctions

There are 4 possible spin states for a two-electron system. These are:

$$\alpha(1)\alpha(2), \beta(1)\beta(2), \alpha(1)\beta(2), \beta(1)\alpha(2)$$

However, only the first two are symmetric or anti-symmetric to electron exchange (which corresponds to exchanging 1 and 2). The last two need to be rewritten as:

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The first three are symmetric, whereas the last one is anti-symmetric.

The triplet state

Say one of the electrons in the helium atom is excited to the 2s state. In this case, its spatial wavefunction will have to be either anti-symmetric (requiring a symmetric spin wavefunction):

$$\Psi_{\text{spatial}} = \psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)$$

Or symmetric (requiring an anti-symmetric spin wavefunction):

$$\Psi_{\text{spatial}} = \psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)\psi_{1s}(2)$$

For anti-symmetric spatial wave function, we see that there are three symmetric spin wave functions.

$$\Psi_{1,0} = \{\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)\} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\Psi_{1,1} = \{\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)\} \alpha(1)\alpha(2)$$

$$\Psi_{1,-1} = \{\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)\} \beta(1)\beta(2)$$

Electrons avoid each other

This set of wave functions corresponds to a triplet state, i.e. it has a spin multiplicity of 3. The triplet state is not allowed in the ground state. In the ground state, the spatial function can only be symmetric and therefore the spin function must be anti-symmetric. However, in this excited state the anti-symmetric spin state,

$$\Psi_{0,0} = \{\psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)\psi_{1s}(2)\} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

is the singlet state. In the limit that

$$\psi_{1s}(1) \approx \psi_{2s}(2)$$

the probability amplitude tends to zero. This means that the electrons are unlikely to be close to each other

Beyond Hydrogen: The Aufbau Principle

In a conceptual way we can imagine using the H atom as model for all atoms. We can populate the hydrogenic orbitals with electrons to create the atoms of the periodic table.

This is not formally correct since we must confront the fact of electron-electron repulsion. However, we can speak of orbital occupancy in this approximation by building up the atoms.

The German word “aufbau” means building up and it refers to this treatment. Thus, we can imagine helium having two electrons in the 1s orbital or a configuration of $1s^2$. Then

We have

Li: $1s^2 2s$ Be: $1s^2 2s^2$ B: $1s^2 2s^2 2p$ C: $1s^2 2s^2 2p^2$

And so on.

Hund's rule

As we populate the p orbitals we must account for the spin pairing energy. The spin pairing energy is minimized by keeping the unpaired electrons at a maximum as shown below:

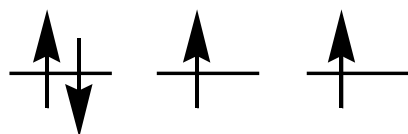
1 electron



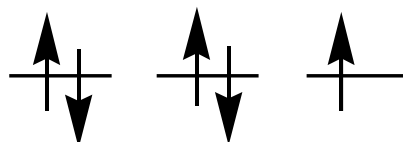
2 electrons



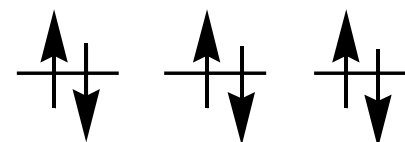
3 electrons



4 electrons



5 electrons



6 electrons

Hund's rule states that the most stable configuration will be the one with the greatest spin multiplicity.

Spin and orbital angular momenta for atoms

The orbital degeneracy is $2\ell + 1$

The spin multiplicity is defined as $2s + 1$.

For N electrons the total value of the angular momentum will be the sum of the individual electronic momenta. The total orbital angular momentum is:

$$L = \ell_1 + \ell_2 + \ell_3 + \dots$$

and the total spin momentum is:

$$S = s_1 + s_2 + s_3 + \dots$$

Term Symbols

The angular momenta result from the configurations possible for the atom. There are actually many configurations possible so it is convenient to summarize the information in a term symbol, which describes the orbital, spin and total angular momentum state of the atom. Term symbols have the form:

$$2S+1L_J$$

Summary

The hydrogen atom is the only atom with an exact solution.

Hydrogen wave functions are used as the approximation for atomic wave functions in multielectron atoms.