AAPT PHYSICS EDUCATION | AMERICAN JOURNAL of PHYSICS

Search for Simplicity: Atoms with several electrons

Victor F. Weisskopf

Citation: American Journal of Physics **53**, 304 (1985); doi: 10.1119/1.14155
View online: http://dx.doi.org/10.1119/1.14155
View Table of Contents: http://scitation.aip.org/content/aapt/journal/ajp/53/4?ver=pdfcov
Published by the American Association of Physics Teachers

Search for Simplicity: Atoms with several electrons

We can use the methods applied to the hydrogen atom in the previous essay for the study of atoms with several electrons. Let us first look at helium. Here we have two electrons with opposite spin in the ground state, considered as a cloud with some kind of average radius R. The energy E is then

$$E \sim -\frac{4e^2}{R} + \frac{e^2}{r_{12}} + 2\frac{\hbar^2}{2mR^2}. \tag{1}$$

The first term is the potential energy of the two electrons in the field of the doubly charged nucleus. The second term is the repulsion between the electrons; the third term represents the kinetic energies of both electrons. Since R and r_{12} appear always in the denominator, we define R^{-1} as the average of the reciprocal distance of the electrons from the center and r_{12}^{-1} as the average of the reciprocal distance between them. We put $r_{12} = R/\beta$ and expect β to be less than unity since r_{12} will be larger than the average distance R from the center. We write the energy (1) in the form

$$E = -\frac{A}{R} + \frac{B}{2R^2}, \quad A = (4-\beta)e^2, \quad B = 2\hbar^2/m. \tag{2}$$

Let us remember once for all—we will need it in later essays also—that the minimum of E and the corresponding R are given by

$$E = -A^2/2B, \quad R = B/A. \tag{3}$$

We find for helium

$$E = -(4-\beta)^2\frac{e^4m}{4\hbar^2}, \quad R = \frac{2}{(4-\beta)}\frac{\hbar^2}{me^2}. \tag{4}$$

How do we find the values of $\beta = R/r_{12}$? Both R and r_{12} depend on the shape of the electron distribution $\rho(r)$, the density of electrons at the distance r from the center. The radius R is defined by $R^{-1} = \int(\rho/r)dx^3$, where $\int dx^3$ is an integration over all space. r_{12} can be found by calculating the electrostatic energy ϵ of two identical electron clouds $\rho(r)$: $\epsilon = e^2/r_{12}$. This calculation is simple but lengthy. The best way to do it is to calculate the electrostatic potential $U(r)$ produced by the charge distribution $e\rho(r)$. Then,

$$\epsilon = e\int dx^3 U(r)\rho(r) = \frac{e^2}{r_{12}}$$

which determines r_{12}. A rectangular charge distribution gives $\beta = 0.8$; an exponential dependence ($\rho \sim e^{-r/b}$) leads to $\beta = 5/8$. The more ρ increases towards the center, the lower is β. Here is something to think about: why is β smaller for distributions packed towards the center? (The answer will appear in the next issue.)

Let us return to helium. The simplest assumption would be a rectangular distribution with $\beta = 0.8$, which gives $E = 5.1$ Ry according to (4). We may use our knowledge that the distribution drops off exponentially with $\beta = 5/8$. Then we get

$$E = -5.7 \text{ Ry}, \quad R = 0.59a_B, \quad \text{Ry} = me^4/2\hbar^2, \tag{5}$$

where a_B ($a_B = \hbar^2/me^2$) is the Bohr radius. The actual energy to remove the two electrons is 5.81 Ry. Again, it is remarkable how close these crude considerations come to the correct results.

We can apply similar methods to the determination of ionization energies and electron affinities of atoms of 3 to 10 electrons. This was done in a paper by M. Kregar and the author which was published in this journal,[1] so that we do not need to repeat it here.

We now turn to atoms with many electrons. We generalize expression (1) to Z electrons around a fixed point charge Ze and assume $Z \gg 1$. This will get us what I like to call "the poor man's Thomas–Fermi method." We get, instead of (1),

$$E = -\frac{Z^2e^2}{R} + \frac{Z(Z-1)}{2}\frac{e^2\beta}{R} + Z\frac{\hbar^2}{2mR^2}\left(\frac{Z}{2}\right)^{2/3}. \tag{6}$$

The first term is the potential energy of Z electrons attracted by the nucleus, and R is an average distance from the center. The second term comes from the repulsion between the electrons. There are $Z(Z-1)/2$ pairs, each giving rise to a potential energy e^2/r_{12}, where $r_{12} = R/\beta$ is an average of the distance between electrons, as we had it in helium. The difference with helium shows up in the kinetic energy. The Pauli principle must be considered when there are more than two electrons. Each electron shares a "private room" of a linear dimension $\tilde{r}$ with a partner of opposite spin. There must be $Z/2$ such rooms within the electron cloud of dimension R, so that $(Z/2)\tilde{r}^3 = R^3$. The minimum kinetic energy per electron is $\sim\hbar^2/(2m\tilde{r}^2)$ which explains the third term in (6).

We may replace $Z(Z-1)$ by Z^2 and get

$$E = -\frac{A}{R} + \frac{B}{2R^2}, \quad A = Z^2e^2\left(1-\frac{\beta}{2}\right),$$

$$B = Z^{5/3}\frac{\hbar^2}{2^{2/3}m}.$$

According to (3), this is a minimum when

$$R = \frac{a_B}{(1-\beta/2)2^{2/3}Z^{1/3}},$$

$$\frac{E}{Z} = -2^{2/3}Z^{4/3}\left(1-\frac{\beta}{2}\right)^2\text{Ry}. \tag{7}$$

We will show below that $\beta = 0.36$, which is much smaller than in helium. This is because the charge distribution is strongly pointed toward the center. With that value we find

$$R = 0.77Z^{-1/3}a_B,$$

$$-\frac{E}{Z} = 1.06Z^{4/3}\text{ Ry} = 14.4Z^{4/3}\text{ eV}. \tag{8}$$

This is the average binding energy of an electron. The actual value is $16\,Z^{4/3}$ eV. The usual Thomas–Fermi method gives $20Z^{4/3}$ eV. Poor man is better than affluent man!

We need the electron distribution $\rho(r)$ in order to determine β. We choose a simple and plausible distribution:

$$\rho = Ae^{-(r/b)}/r^n. \tag{9}$$

Electron densities are expected to exhibit an exponential decrease, albeit not as simply as in (9). The factor r^{-n} is included in order to assure that ρ has the correct behavior near the center: There should be about two electrons within the radius $r_K = a_B/Z$ of the K-shell, a number which is independent of Z. (The S-states of outer shells contribute a negligible amount.) The three constants A, b, n in (9) are

determined by the following conditions imposed on ρ:

$$4\pi\int_0^\infty \rho r^2\,dr = Z, \quad 4\pi\int_0^{a_B/Z} \rho r^2\,dr = \text{“2”},$$

$$4\pi\int_0^\infty \rho r\,dr = \frac{Z}{R}. \tag{10}$$

The first condition assures that there are Z electrons; the second determines the number of electrons with the K-shell. The symbol "2" is used because we only need this number to be independent of Z and near 2. The third condition assures the average of r^{-1} for each electron is R^{-1} as used in (6).

We do not show the details of the simple integrations (10). One determines A from the first integral; the condition that the second should be independent of Z determines n; the third integral is used to express b in terms of R. The results of (10) turn out to be

$$4\pi A = 2Z/(\pi^{1/2}b^{3/2}), \quad n = 3/2, \quad b = 2R. \tag{11}$$

We obtain β for the distribution (9) with the constants (11) by using the methods mentioned before. The calculations are even lengthier than those for the simpler distributions which we considered for helium, but there is no fundamental difficulty. The result turns out to be $\beta = 1 - 2/\pi = 0.36$, the value which we used in (7) to determine the energy of the atom and the length R.

We can use the electron distribution (9) to get an idea of the atomic size. The magnitude R is not the radius R_a of the atom; it is the average distance of the electrons from the center and, therefore, much smaller than R_a since most of the electrons are in the inner parts. In order to get an estimate of the size of the atom, we must find out the extension of the distribution (9). Literally, it goes to infinity, but we may get a rough value of the atomic radius R_a by finding the radius at which, say, one half of the last electron is left outside. This distance indicates where the last electron may be found. In other words, R_a is given by the integral

$$4\pi\int_{R_a}^\infty \rho r^2\,dr = \frac{1}{2}. \tag{12}$$

Table I. Estimates of atomic radii.

Z	y	R_a/a_B
30	10.04	2.49
50	11.16	2.33
90	12.42	2.13

The evaluation of this integral leads to the following equation for $y = R_a/R$:

$$2\pi/(4Z)^2 = ye^{-y}.$$

We then obtain, for three values of Z, the radii found in Table I. The atomic radius turns out to be almost independent of Z. The decrease of R as $Z^{-1/3}$ is compensated for by the fact that the exponentially decaying ρ must reach farther out to get to the last electron. One should conclude from this result only that atomic radii do not depend much on Z and are of the order of a few Bohr radii. The slight decrease of R_a in Table I is not a real effect; it comes from the simple exponential form (9) of the electron distribution. Actually, the exponential decrease is much sharper near the center than farther away, because the effective charge of the core is higher for the inner electrons. This effect is more pronounced for higher Z and has a strong influence on the determination of R_a by the integral (12). It would increase the radii.

The homework to this essay, of course, is to perform the indicated calculations of the constants (11), of the β values for the different distributions, and of R_a.

Victor F. Weisskopf

[1]M. Kregar and V. F. Weisskopf, Am. J. Phys. **50**, 213 (1982).

Addendum: The ideas presented in the January essay have been published as early as 1858 by J. J. Waterton [Philos. Mag. **15**, 1 (1858)] as pointed out by A. P. French [Am. J. Phys. **35**, 162 (1967)].

PROBLEM

A cylindrical solid of any convex shape is rolling *under gravity* on horizontal plane. The potential energy $V(s)$ can be represented[1] by $V(s) = mg[\mathbf{r}(0)\mathbf{n}(0) - \mathbf{r}(s)\mathbf{n}(s)]$, where $\mathbf{r}(s)$ is the radius vector connecting the center of mass G of the rolling solid of mass m to the contact point M, $\mathbf{n}(s)$ is the inner normal, s is the curvilinear coordinate ($s = 0$ corresponds to the equilibrium at a point M_0), and g is the gravity constant.

Find all curves $\mathbf{r}(s)$ such that $V(s)$ is identically zero [such that $-\mathbf{r}(s)\mathbf{n}(s) = -\mathbf{r}(0)\mathbf{n}(0) = +h = \|G\mathbf{M}_0\|$]. (Solution is on page 349.)

[1]A. Ronveaux, Am. J. Phys. **52**, 618 (1984).