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IONIZATION ENERGIES AND ELECTRON AFFINITIES
OF ATOMS UP TO NEON

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A B S T R A C T

An elementary method is presented for
the determination of the binding energies
of electrons in the L shell.

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With today's modern computers it is possible to calculate the energies of simple atoms and ions with any desired accuracy by using numerical approximations to the solutions of the Schrödinger equation for N electrons in the Coulomb field of the nucleus and the field of their mutual repulsions. In this paper we are going to use very simple methods to calculate the energies of atoms and ions up to neon in order to show how a simple approach can achieve a remarkable accuracy in determining ionization energies and electron affinities. The method also serves to illuminate the important factors that determine the electron energies within atoms.

1. HYDROGEN AND HELIUM

We start with the simplest atoms in order to describe our method. Consider one electron in a Coulomb field. We characterize the lowest quantum state of the electron by one number only: by its spatial dimension R . Then the potential energy V will be of the order of magnitude

$$V \approx -\frac{e^2}{R} \quad (1)$$

The kinetic energy K can be estimated by arguing that the electron wavelengths λ involved in a wave function spreading over a region of the order R must be in the average^{*)} $\lambda \sim R$. This corresponds to a momentum $p \sim \hbar/R$ and therefore the kinetic energy is of the order $p^2/2m$:

$$K \approx \frac{\hbar^2}{2mR^2} \quad (2)$$

The total energy therefore is approximately

$$E = -\frac{e^2}{R} + \frac{\hbar^2}{2mR^2} \quad (3)$$

Since we will use frequently equations of this form let us write it in the form

$$E = -\frac{A}{R} + \frac{B}{2R^2} \quad (4)$$

^{*)} In such estimates it is much better to use $\lambda = \lambda/2\pi$ for a wavelength, and $\hbar = h/2\pi$ for Planck's constant.

We then determine at which R the energy E assumes a minimum value E_0 and we find

$$R = \frac{B}{A}, \quad E_0 = -\frac{A^2}{2B}. \quad (5)$$

For the hydrogen case we get:

$$R = \frac{\hbar^2}{me^2} \equiv a = 5.3 \times 10^{-9} \text{ cm}$$

$$E_0 = -\frac{me^4}{2\hbar^2} \equiv -Ry = -13.6 \text{ eV}. \quad (6)$$

a is the Bohr radius and Ry is the Rydberg unit of energy. Our order of magnitude estimate gives us the exact energy value of the hydrogen ground state, and a good value -- the Bohr radius -- for the size of the quantum state.

This method tells us that the ground state in hydrogen is a balance between two tendencies: the Coulomb attraction tends to make it small, but the kinetic energy tends to keep it large since a smaller wave function implies smaller wavelength and, therefore, higher momentum and kinetic energy. The quantum effects "resist" the compression to smaller volumes since this would imply a higher energy. The atom is the balance between Coulomb attraction and quantum resistance to compression.

Let us try to apply this method to an excited state. The potential energy, of course, remains to be of the form (1) but the kinetic energy will be different because, in excited states, there are nodes in the wave function. Thus the characteristic wavelength λ will be R/n where $(n-1)$ is the number of nodes. Then we get

$$K \approx \frac{\hbar^2 n^2}{2m R^2}. \quad (7)$$

Changing the expression (3) accordingly for the energy gives:

$$A = e^2, \quad B = \frac{n^2 \hbar^2}{m} \quad (8)$$

and, therefore, from (4)

$$R = n^2 a, \quad E_0 = - \frac{m e^4}{2 n^2 \hbar^2} = - \frac{1}{n^2} R_y \quad (9)$$

Again we find the energy exactly correct. The dimension of the excited states is n^2 times larger than the ground state.

We now come to the helium atom. Here two electrons occupy the ground state^{*)}; thus the kinetic energy is twice the expression (3); the potential energy of the nuclear attraction is now four times the expression (1), twice because the charge of the nucleus is double, and twice because there are two electrons. Furthermore, there is an additional term V_{ee} coming from the repulsion between the two electrons which is of the form

$$V_{ee} \approx k \frac{e^2}{R}$$

where r/k is the average distance between the electrons. We expect R/k to be larger than R since the electrons can also be on opposite sides. We then get

$$E = - \frac{(4-k)e^2}{R} + 2 \frac{\hbar^2}{2mR^2} \quad (10)$$

and

$$E_0 = - \frac{(4-k)^2}{2} R_y.$$

Actually $E_0 = 5.70 R_y$ so that $k = 0.625 = 5/8$.

The value of k can also be calculated directly. We need only to assume that their dependence of the charge density of each of the electrons is exponential:

$$\rho = A e^{-\frac{r}{b}}. \quad (11)$$

We determine A from the fact that the space integral over ρ must give e and get

^{*)} with opposite spin in order to satisfy the Pauli principle.

$$A = e \frac{1}{8\pi \ell^3}$$

We get a connection between b and R by requiring that the average radius of ρ be R . Since R figures in the potential energy as R^{-1} , it is useful to define R such that R^{-1} is the average of r^{-1} with the distribution (11):

$$\frac{1}{R} = \frac{1}{2} \int_0^{\infty} \frac{\rho(r)}{r} 4\pi r^2 dr \quad (12)$$

where the factor $4\pi r^2 dr$ comes from the integration over all space. Inserting (11) into (12) results in

$$R = 2b \quad (13)$$

The calculation of the electrostatic energy V_{ee} between two identical charge densities (10) (the two electrons) is a relatively easy task. It is done in the Appendix with the result:

$$V_{ee} = \frac{5}{16} \frac{e^2}{b} = \frac{5}{8} \frac{e^2}{R} \quad (14)$$

in agreement with the value determined from the observed energy of the helium ground state.

2. THE L-SHELL ATOMS

When the number of electrons is larger than two the additional electrons must be placed in higher states than the one occupied in H and He (K-shell). The next higher states are in the L-shell, containing states with one node ($n = 2$ in (3)). There is room for eight electrons in the L-shell; two go into the 2s-state (zero orbital angular momentum) and six into the three 2p-states (orbital angular momentum 1). We will call them $2p_x$, $2p_y$, $2p_z$.

What is the energy of the atom when N electrons ($N \leq 8$) are in the L-shell? The kinetic energy follows expression (3) and we get

$$K = 4N \frac{\hbar^2}{2mR^2} \quad (15)$$

Now we come to the potential energy. We use the assumption that the nucleus and the two electrons in the K-shell act as a central point charge $Z'e$ where $Z' = Z - 2$, Z being the atomic number. This assumption will be a good one for the 2p-states, since their wave functions go to zero near the centre, as in all states with $l \neq 0$. It will not be a good assumption for the 2s-state. That state does not go to zero at the centre; it corresponds to a "penetrating orbit". We therefore use a larger effective charge for the 2s-state, namely $Z'' = Z - 2f$ where $f < 1$. It will turn out that $f = 0.8$ gives good results.

The potential energy of an atom with a nuclear charge Z and with N electrons in the L-shell (N does not contain the two electrons of the K-shell) is then

$$\begin{aligned} V &= -\frac{e^2}{R} N Z'' + V_{ee} && \text{for } N < 2 \\ V &= -\frac{e^2}{R} [2Z'' + (N-2)Z'] + V_{ee} && \text{for } N > 2 \\ Z' &= Z - 2, \quad Z'' = Z - 2f; \end{aligned} \quad (16)$$

V_{ee} is the energy of the mutual repulsion between the N electrons. It would be tempting to set

$$V_{ee} = \frac{N(N-1)}{2} \frac{ke^2}{R} \quad (17)$$

since $N(N-1)/2$ is the number of pairs and ke^2/R is the repulsion between two electrons as we found it in helium. The resulting radius R would be a good deal larger than in helium since the kinetic energy of $n = 2$ states has a much stronger expanding effect (remember that the radius of the $n = 2$ state in hydrogen is four times larger than the ground state). But expression (17) is too simplistic for our use; it does not reproduce the fine changes in the ionization energies and affinities as functions of Z and N . We can improve (17) by the following observation. The states in the L-shell are not all equal and, therefore, the repulsion energy of an electron pair will depend on the states in which the two electrons sit.

Remember that the 2s-states are spherically symmetric and that the three substates $2p_x$, $2p_y$, $2p_z$ can be considered as rotationally symmetric figure-eight patterns^{*)} around the three axes (see Fig. 1). We then distinguish three types of electron pairs in the L-shell:

strongly interacting pairs

These are the pairs where both electrons are in the same 2p-states. In this case the electrons will be rather near to each other.

weakly interacting pairs

These are the pairs where the electrons have parallel spin and also the pairs in two different p-states, whatever the relative spin orientation. Parallel spins keep electrons apart, and two different p-states have relatively little overlap; thus the electrons will be relatively far from each other.

normally interacting pairs

These are the pairs where both electrons are in the s-state or one in an s-state and the other in one of the p-states with opposite spin.

The filling of the L-shell takes place such that the s-state is filled first -- it has a lower energy than the p-states because of $Z'' > Z'$. In filling the p-states one puts as many electrons as possible in different p-states because this procedure lowers the repulsive effects (it maximizes the weak pairs). Let us call n , s , w the number of normal strong or weak pairs respectively. It is easily seen that

$$\begin{aligned} n &= N - 1 \\ s &= \begin{cases} 0 & \text{for } N \leq 5 \\ N - 5 & \text{" } N > 5 \end{cases} \\ w &= \begin{cases} \frac{(N-1)(N-2)}{2} & \text{for } N \leq 5 \\ \frac{(N-2)(N-3)}{2} + 3 & \text{" } N > 5 \end{cases} \end{aligned} \quad (18)$$

^{*)} In the usual presentation one uses the three spherical harmonics $Y_{j,m}$, $j = 1$, $m = -1, 0, +1$ for these states. Then only $Y_{1,0}$ has the figure-eight shape around the z-axis. However, the linear combinations $Y_{1,1} + Y_{1,-1}$ or $1/i(Y_{1,1} - Y_{1,-1})$ have the same shape around the x and y axis respectively and correspond to p_x and p_y .

Table 1 gives the numbers n, w, s for different N . The repulsion energy V_{ee} can now be written in the form

$$V_{ee} = \frac{ke^2}{R} (n + aw + bs), \quad a < 1, b > 1. \quad (19)$$

There are good reasons to assume

$$\frac{2a + b}{3} = 1 \quad (20)$$

To make (20) plausible we conclude as follows. The average of the three p-states has a spherically symmetric charge distribution. We write this average as $\frac{1}{3}(p_x + p_y + p_z)$. We expect that the interaction of one p-state with that average would be "normal"; we call it I_n . We denote the interaction between two states p_i, p_j by $[p_i p_j]$; then

$$I_n = \frac{[p_i p_x] + [p_i p_y] + [p_i p_z]}{3}$$

where i is x, y or z . Now $[p_i p_i]$ would give strong interaction I_s , whereas $[p_i p_j]$ ($j \neq i$) would give a weak one I_w . Hence $I_n = \frac{1}{3}[I_s + 2I_w]$ from which follows the relation (20).

Now we are able to write down the complete expression for the energy E of an atom with a nuclear charge Z and N electrons in the L-shell. With the use of (15), (16) and (19) we get

$$E = -\frac{A}{R} + \frac{B}{2R^2} \quad (21)$$

with

$$A = \begin{cases} e^2 [NZ'' - kn] & \text{for } N \leq 2 \\ e^2 [2Z' + (N-2)Z' - k(n + aw + bs)] & \text{for } N > 2 \end{cases}$$

and

$$B = 4N \frac{\hbar^2}{m}$$

Z'' and Z' are given in (16).

The minimum energies E_0 are [see Eq. (5)]:

$$E_0 = \begin{cases} -\frac{[NZ'' - nk]^2}{4N} & \text{for } N \leq 2 \\ -\frac{[2Z'' + (N-2)Z' - k(n + aw + bs)]^2}{4N} & \text{for } N > 2 \end{cases} \quad (22)$$

All numbers in (21) or (22) are defined with the exception of the three parameters k , f and a ; b is given by a according to (20).

It turned out that the best results are obtained with

$$f = 0.8, \quad a = 0.9, \quad b = 1.2, \quad k = 0.64. \quad (23)$$

A comment about k is in place. We have seen in the discussion of helium that the interaction constant k is 0.625 for two electrons in the ground state with a charge distribution (10). The L-state charge distributions will be similar to (11) but not exactly the same. We expect that they are less "pointed" in the centre compared to (11). It is shown in the Appendix that a less pointed distribution increases somewhat the value of k . It is therefore not surprising that the best k for the L-shell is a little higher than the one for the K-shell. Table 2 shows the total binding energies $-E_0$ for all atoms and their positive and negative ions from $Z = 3$ (lithium) to $T = 10$ (neon). The numbers in brackets are the observed values. The agreement is extremely good.

A much more severe test is the comparison of the calculated ionization energies and electron affinities with the observed ones. These are differences between the binding energies with the same Z but with values of N that differ by one unit. The electron affinity of an atom with atomic number Z is defined as

$$U = E_0(Z, Z-2) - E_0(Z, Z-1) \quad (24)$$

where $E_0(Z, N)$ is the energy for an atom with N electrons in the L-shell.

Note that $-E_0(Z, Z-2)$ is the total binding energy of all electrons in the neutral atom, whereas $-E_0(Z, Z-1)$ is the same magnitude for the negative ion. We distinguish different ionization energies I_t where t is usually denoted by a Roman number. I_t is the energy necessary to take an electron away from a positive ion of the charge $t - 1$. For example, I_I is the ionization energy of the neutral atom, I_{II} is the ionization energy of the positive ion of charge unity, etc. We get

$$I_t = E_0(Z, Z-2-t) - E_0(Z, Z-1-t) \quad (25)$$

Table 3 gives the results of the affinities and the ionization energies of all elements from lithium to neon as calculated from (22), (24) and (25), with the constants (23). The numbers in brackets are the observed values. We find a good semi-quantitative agreement, even for these differences. This is seen also in the graphs shown in Fig. 2 and Fig. 3. The former figure shows the plot of the ionization energies I_{II} to I_{VIII} ; the latter figure shows, on an expanded scale, I_I and the affinities U .

It is not surprising that the ionization energies increase with increasing Z . After all, the higher Z , the greater is the Coulomb attraction that binds the last electron, in spite of increasing repulsion by the other electrons. It is interesting to analyse the reasons for the drop of I_I from Be to B and then from N to O. The third electron in the L-shell is no longer in the 2s-state, it therefore does no longer enjoy the higher central charge Z'' . It is attracted only by Z' . Therefore, its bond is relatively weaker. The sixth electron is the first one that forms a pair with strong repulsion as Table 1 shows; this is why it is less bound than average. We can also understand the dips of electron affinity for Be and N. Indeed, the affinities for those two atoms are negative; it means an additional electron would not be bound. The reasons are similar to our arguments for the dips in ionization energy. The additional electron to the Be-atom would be in a p-state which is less bound because $Z' < Z''$. In the case of N, the additional electron is the first that forms a strong repulsion pair. This is why those additional electrons will not be bound by the neutral atoms.

It is astonishing that one can get satisfactory quantitative results with such primitive methods that use hydrogen -- like wave functions in spite of the interactions between electrons. This is a property of all ensembles in which a large number of particles occupy the lowest states in an exterior potential. Then the interaction between the particles does not much deform the shapes of the occupied states; they remain more or less in the form ψ_i they would have had

without any interaction. The reason for this is easy to see. A change of a wave function ψ_i is equivalent to adding to it other wave functions that are orthogonal to ψ_i . Occupied wave functions, however, cannot be used; it would violate the Pauli principle. Only the unoccupied ones are available for such changes. These are, however, energetically higher up, a fact that reduces the amplitudes of the corrections to ψ_i . This is why an ensemble of particles, occupying the lowest states of an exterior potential, is rather stable against changes due to interactions between the particles. In our case, the exterior potential was the Coulomb field of the nucleus. Another example is the configuration of nucleons in a nucleus. Here the exterior potential is the average nuclear force in the form of a potential trough. Our principle explains the astonishing validity of the single particle shell-model in nuclei in spite of the strength of inter-nucleon forces. A third example is the electron gas in a metal. Here the exterior potential is the potential box representing the piece of metal. The interactions between the electrons do not appreciably reduce the validity of the free-electron model^{*)}.

^{*)} See V.F. Weisskopf, Science 113 (1951) 2926 or V.F. Weisskopf, Physics in the XX century, M.I.T. Press (1972)

APPENDIX

We want to calculate the electric repulsion energy V_{ee} between two electrons, each distributed in space according to a given charge density $\rho(r)$. We first calculate the electrostatic potential $\phi(r)$ due to this charge density. Then the electrostatic energy is given by the integral

$$V_{ee} = \int \phi(r) \rho(r) 4\pi r^2 dr. \quad (A.1)$$

The potential $\phi(r)$ is given by the Poisson equation

$$\nabla^2 \phi = -4\pi \rho$$

Since everything depends only on r , we can write

$$\frac{1}{r} \frac{d^2(r\phi)}{dr^2} = -4\pi \rho(r)$$

It follows from this that

$$\frac{d}{dr}(r\phi) = F(r) + C, \quad F(r) = 4\pi \int_r^\infty \rho(r) dr \quad (A.2)$$

C is an integration constant. Further integration gives

$$(r\phi) = - \int_r^\infty F(r) dr + Cr + D$$

where D is a second integration constant. Finally

$$\phi = \frac{e}{r} - \frac{1}{r} \int_r^\infty F(r) dr \quad (A.3)$$

We expect $\phi \rightarrow e/r$ for $r \rightarrow \infty$; hence $C = 0$ and $D = e$. We then calculate V_{ee} by inserting (A.3) into (A.1).

With the charge density (11) we obtain for $F(r)$ as defined in (A.2):

$$F(r) = \frac{e}{2b} \left(1 + \frac{r}{b} \right) e^{-\frac{r}{b}}$$

and then from (A.3) and (A.1):

$$V_{ec} = \frac{5}{16} \frac{e^2}{b} = \frac{5}{8} \frac{e^2}{R} \quad (A.4)$$

as in (14), where $R^{-1} = \langle r^{-1} \rangle$.

It is of interest to see what one gets with a uniform charge distribution up to a maximum radius r_0 :

$$\rho = \begin{cases} A & \text{for } r < r_0 \\ 0 & \text{for } r > r_0 \end{cases} \quad A = \frac{3e}{4\pi r_0^3} \quad (A.5)$$

Then we obtain

$$F(r) = \frac{3}{2} \frac{e}{r_0} \left[1 - \left(\frac{r}{r_0} \right)^2 \right]$$

and

$$\phi = \frac{3}{2} \frac{e}{r_0} - \frac{1}{2} e \frac{r^2}{r_0^3} \quad r < r_0$$

This gives

$$V_{ec} = \frac{6}{5} \frac{e}{r_0}$$

In order to compare this with (A.4) we must determine $\langle r^{-1} \rangle$ with the distribution (A.5). We find $R^{-1} = \langle r^{-1} \rangle = \frac{3}{2} r_0^{-1}$. Therefore we get

$$V_{ee} = \frac{4}{5} \frac{e^2}{R}$$

Here the factor of $1/R$ is somewhat larger than with the exponential charge distribution (11). This shows that a flatter, less "pointed" distribution gives rise to a larger coefficient of R^{-1} in V_{ee} .

Table 1

occupation of							
N	s	p _x	p _y	p _z	n	w	s
2	2	0	0	0	1	0	0
3	2	1	0	0	2	1	0
4	2	1	1	0	3	3	0
5	2	1	1	1	4	6	0
6	2	2	1	1	5	9	1
7	2	2	2	1	6	13	2
8	2	2	2	2	7	18	3

Table 2

Z \ N	1	2	3	4	5	6	7	8
3	0.49 (0.40)	0.58 (0.44)	0.34					
4	1.44 (1.34)	2.16 (2.02)	2.06 (2.00)	1.70				
5	2.89 (2.79)	4.74 (4.64)	5.28 (5.25)	5.28 (5.28)	4.83			
6	4.84 (4.74)	8.32 (8.26)	10.01 (10.05)	10.851 (10.88)	10.97 (10.97)	10.26		
7	7.29 (7.20)	12.90 (12.89)	16.23 (16.38)	18.42 (18.56)	19.62 (19.63)	19.58 (19.61)	18.84	
8	10.24 (10.16)	18.48 (18.53)	23.95 (24.22)	28.00 (28.26)	30.76 (30.84)	31.90 (31.84)	32.06 (31.95)	31.36 (31.46)
9	13.69 (13.62)	25.06 (25.17)	33.17 (33.57)	39.58 (39.98)	44.40 (44.59)	47.23 (47.16)	48.78 (48.44)	49.18 (48.70)
10	17.64 (17.58)	32.64 (32.82)	43.90 (44.43)	53.15 (53.71)	60.54 (60.85)	65.55 (65.52)	68.99 (68.53)	71.01 (70.11)

Table 3

$k = 0.32$ $q = 0.9$ $b = 1.2$ $f_s = 0.8$

	electron affin.	I	II	III	IV	V	VI	VII	VIII
Li	1.26 (0.6)	6.66 (5.39)							
Be	-1.35 (-0.11)	9.83 (9.32)	19.58 (18.21)						
B	-0.15 (10.3)	7.38 (8.30)	25.2 (25.2)	39.3 (37.9)					
C	1.70 (1.24)	11.46 (11.26)	22.9 (24.4)	47.4 (47.9)	65.8 (64.5)				
N	-0.53 (-0.2)	16.2 (14.5)	29.9 (29.6)	45.2 (47.5)	76.3 (77.5)	99.1 (97.9)			
O	2.06 (1.47)	15.5 (13.6)	37.5 (35.1)	55.1 (54.4)	74.4 (77.4)	112.1 (113.4)	139.2 (138.1)		
F	5.47 (3.5)	21.0 (17.4)	38.4 (35.0)	65.6 (62.7)	87.1 (87.1)	110.3 (111.2)	154.6 (157.1)	186.2 (185.2)	
Ne		27.3 (24.6)	46.8 (41.0)	68.1 (63.5)	100.5 (99.1)	125.9 (126.2)	153.0 (157.9)	204.0 (207.3)	239.9 (239.0)

TABLE CAPTIONS

- Table 1 : Numbers of different pairs in the L-shell.
- Table 2 : L-shell binding energies $-E_0$ in R_y -units, for different Z and N.
The experimental values are given in brackets.
- Table 3 : Electron affinities and ionization energies in the L-shell.

FIGURE CAPTIONS

- Fig. 1 : A sketch of the square of a $2p_z$ -wave function. It is rotationally symmetric around the z-axis. The circles are lines of equal density. The p_x - and p_y -wave function give the same figure along the x- and y-axis.
- Fig. 2 : Calculated and observed ionization energies I_{II} to I_{VIII} for the L-shell elements.
- Fig. 3 : Calculated and experimental first ionization energies and electron affinities for the L-shell elements.

FIG. 1

FIG. 2

FIG. 3