

Chapter 4

Effects of the Nucleus on Atomic Structure

Until now we have discussed atoms as if the nuclei were point charges with no structure and infinite mass. Real nuclei have finite mass, possibly non-zero angular momentum, \mathbf{I} , and a charge which is spread out over a finite volume. As a result, they possess magnetic dipole moments and electric quadrupole moments coupled to the angular momentum, and possibly higher moments as well. All of these properties affect the atomic energy levels at a level about 10^{-5} rydberg. Here's a catalog of these effects:

Cause	Result	How Observed
Finite Mass	Mass Shift	Isotope shifts
Finite Volume of Charge	Volume Shift	
Magnetic Dipole ($I \geq 1/2$)	Hyperfine structure	Energy splittings
Electric Quadrupole ($I \geq 1$)	Hyperfine structure	

The first two effects produce only a small shift of the spectral line, and thus the only quantity accessible to measurement is the variation of the line position between different isotopes of the same element. (In atoms with only one or two electrons it may be possible to predict the position of a line with significant accuracy to deduce the isotope shift absolutely.) Laser spectroscopy makes it possible to measure isotope shifts to at least 10^{-9} Ry or $10^{-3} - 10^{-4}$ of the shift.

The moments of the nucleus couple to its spin which interacts with the angular momentum of the rest of the atom. This splits the energy levels of the atom according to the magnitude $|\mathbf{F}|$, where $\mathbf{F} = \mathbf{I} + \mathbf{J}$. The resulting hyperfine structure can be measured with almost limitless precision (certainly $< 10^{-18}$ Rydberg) using the techniques of RF spectroscopy. Hyperfine transitions in Cs and H are currently the best available time and frequency standards. Generally speaking, magnetic dipole interactions predominate in atoms and electric quadrupole interactions in molecules.

With the exception of the mass shift, the manifestations of nuclear structure in atomic spectra provide important information on the static properties of nuclei which are among the most precise information about nuclei. Unfortunately the great precision of the atomic measurements is generally lost in deducing information about nuclear structure because the core electrons affect the magnetic and electric interactions of the valence electrons with the nucleus.

4.1 Allowable Multipole Moments in Nuclei

4.1.1 Introduction

In general, nuclei are composed of more than one particles, and hence it is possible for nuclei to have multipole moments beyond electric monopole and magnetic dipole. Multipole moments of a nucleus arise from its angular momentum I , and the allowed moments are governed by both I and symmetry consideration. In this section, we discuss what are the possible multipole moments for nuclei. We

shall denote the order of multipoles as follow: monopole $l = 0$, dipole $l = 1$, quadrupole $l = 2$, octopole $l = 3$, etc.

4.1.2 Angular Momentum and Multipole Moments

The multipole moment of a nucleus arises from its angular momentum. To see that, intuitively we know that multipole moment is a consequence of shape. In order to distinguish shapes, one needs be able to distinguish orientation, and it is angular momentum that sets orientation. For example, let us consider a magnetic dipole. In order to measure it, one needs to be able to distinguish between up and down direction, which can be accomplished by passing the dipole through a uniform field and observing whether it moves up or down (Stern-Gerlach experiment).

Q: What is the minimum I for dipole moment?

A: As discussed above, in order to oberseve dipole moment, one needs to be able to distinguish up and down. Quantum mechanically, the dipole moment results in two energy levels different from the single energy level of a monopole. This implies one needs to have at least $I = 1/2$.

Q: What is the minimum I for quadrupole moment?

A: Quadrupole moment is basically an ellipse. In order to tell that one has an ellipse, one needs to be able to distinguish not just up and down, but also an orthogonal orientation. It implies three energy levels, and hence $I = 1$.

In general, in order to possess a moment of order l , a nucleus needs to have at least $l \leq 2I$.

Formally, let us denote the multipole operator as $T_{l,m}$, where l is the angular momentum quantum number of the multipole, and m is the azimuthal quantum number. In coordinate space, $T_{l,m}(r, \theta, \phi) = r^l Y_{l,m}(\theta, \phi)$ is the solid harmonics, with $Y_{l,m}$ the spherical harmonics. The moment of the nucleus is then given by $\langle I, m | T_{l,m} | I, m \rangle$. Now, we know the component involving azimuthal quantum number decouples from the angular quantum numbers: $\langle I, m | T_{l,m} | I, m \rangle = \langle I | T_l | I \rangle \langle m | T_m | m \rangle$. Whether the angular component has non-zero value tells us whether the particular moment is forbidden given the I . Specifically, one can pick $T_l = Y_{l,0}(\theta)$. The angular dependence of the first few $m = 0$ spherical harmonics are given here:

$$Y_{0,0} \propto 1 \quad (4.1)$$

$$Y_{1,0} \propto \cos \theta \quad (4.2)$$

$$Y_{2,0} \propto (3 \cos^2 \theta - 1) \quad (4.3)$$

Graphically, one can imagine the "triangle rule". Consider a vector \mathbf{l} , and asks how can one add \mathbf{I} to get \mathbf{l} . It is possible only when $|\mathbf{I}|$ is at least $|\mathbf{l}|/2$. And hence one also obtains the same condition $l \leq 2I$.

4.1.3 Symmetry Consideration

Besides angular momentum consideration, parity symmetry further restricts what specific electric and magnetic multipoles are allowed in a nucleus. Let us begin with an example: can a nucleus possesses a permanent electric dipole

moment? Assuming an electric dipole moment \mathbf{d} is possible, let us apply parity transformation on the nucleus. Electric dipole moment has odd parity and thus changes sign. Therefore, a permanent electric dipole moment is forbidden by parity symmetry. On the other hand, a magnetic dipole moment does not change sign under parity transformation and thus is allowed.

In general, the parity of the multipoles is as follow:

Electric multipole of order l : $(-1)^l$

Magnetic multipole of order l : $(-1)^{l+1}$

Therefore, we see that even electric multipoles ($l = 0$ monopole, $l = 2$ quadrupole, ...) and odd magnetic multipoles ($l = 1$ dipole, $l = 3$ octopoles, ...) are the only allowed multipole moments.

In summary, we see that symmetry consideration allows a nucleus to have even electric multipoles and odd magnetic multipoles. In addition to these restrictions, angular momentum consideration limits the multipole orders to $l \leq 2I$.

4.2 Hyperfine interaction

4.2.1 Introduction

Hyperfine structure, as its name suggests, is extremely small on the scale of atomic interactions. To give an idea of its size, note that fine structure, which arises from relativistic effects and the spin-orbit interaction, is $O(\alpha^2)$ (i.e. of order α^2 on the scale of atomic interactions). The magnetic hyperfine interaction, which arises from the interaction of the nuclear magnetic moment with the surrounding electrons, is $O(\alpha^2 m_e/M_p)$, which is approximately 1000 times smaller. Nevertheless, studies of hyperfine structure have played an important role in the determination of nuclear properties. Perhaps more relevant today is the role of hyperfine structure in many laser-atomic experiments, particularly those that involve manipulating atoms with light. This is because hyperfine structure affects the optical selection rules and the transfer of momentum and angular momentum to atoms by light. The magnetic hyperfine interaction is most important for atoms with an unpaired electron. Consequently, the alkali-metal atoms, which are the workhorses for laser-atomic physics, all display prominent hyperfine structure, sometimes to the despair of the experimenter.

The fact that the nucleus is a charge cloud with angular momentum suggests the possibility that it might possess magnetic and electric moments. Time reversal and parity invariance restrict the possible magnetic moments to dipole, octopole, ... and the possible electric moments to monopole ($Q = Ze$), quadrupole... The magnetic dipole and electric quadrupole interactions are dominant in the hyperfine interaction.

The magnetic dipole moment can be measured only if the nucleus has $I \geq 1/2$, and it splits only those levels for which $J \geq 1/2$. Similarly, the electric quadrupole interaction is observable only when I and J are both ≥ 1 .

Note that the units used in this section are ESU.

4.2.2 Classical analysis of the magnetic hyperfine interaction

The magnetic moment of the nucleus is generally expressed in terms of the nuclear magneton,

$$\mu_N = \frac{e\hbar}{2M_P c} \quad (4.4)$$

and the nuclear g-factor, g_I

$$\mu = g_I \mu_N I. \quad (4.5)$$

In some cases it is convenient to express the nuclear moment in terms of the Bohr magneton. This is done by defining the g-factor g_I' by

$$\mu = g_I' \mu_B I. \quad (4.6)$$

To emphasize the fact that the nuclei are complex particles we note that the g-factors of the neutron and proton are

$$g_P = +5.586 \quad g_N = -3.826, \quad (4.7)$$

neither one of which is close to a simple integer.

The magnetic moment of the nucleus couples to the magnetic field produced at the nucleus by the electrons in the atom. As a result \mathbf{J} and \mathbf{I} are coupled together to form \mathbf{F} , the total angular momentum of the entire atom

$$\mathbf{F} = \mathbf{J} + \mathbf{I} \quad (4.8)$$

The magnetic coupling between \mathbf{J} and \mathbf{I} adds a term to the Hamiltonian for the magnetic dipole hyperfine structure which is the interaction between a nucleus with magnetic moment μ_I , and the magnetic field \mathbf{B}_J due to a single valence electron.

$$H = -\mu_I \cdot \mathbf{B}_J \quad (4.9)$$

The electron's magnetic field is proportional to its angular momentum \mathbf{J} , and so we can write $H = a\hbar \mathbf{I} \cdot \mathbf{J}$ (4.10) Writing $\mathbf{I} \cdot \mathbf{B}_J$ as $(\mathbf{I} \cdot \mathbf{J})(\mathbf{J} \cdot \mathbf{B}_J)/J^2$, we have

$$a\hbar = -\frac{\mu_I}{I} < \frac{\mathbf{J} \cdot \mathbf{B}_J}{J^2} > \quad (4.11)$$

The constant a is called the hyperfine coupling constant. By convention, it is written in units of frequency.

There are two contributions to \mathbf{B}_J , orbital and spin: $\mathbf{B}_J = \mathbf{B}_L + \mathbf{B}_S$. We shall first evaluate the fields classically. The magnetic moment of the electron is given by

$$\mu_e = -g_e \mu_B \mathbf{S} \quad (4.12)$$

where μ_B is the Bohr magneton. (The negative sign is taken by convention, so that $g_e \sim 2$ is a positive number.) Then,

$$\mathbf{B}_L(0) = \int \frac{I d\mathbf{s} \times \hat{\mathbf{r}}}{r^2} \rightarrow -e\mathbf{v} \times \left(\frac{-\mathbf{r}}{r^3} \right) = -2\mu_B \frac{\mathbf{L}}{r^3} \quad (4.13)$$

$$\mathbf{B}_S(0) = -\frac{1}{r^3} [\mu_e - 3(\mu_e \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}] = +g_e \frac{\mu_B}{r^3} [\mathbf{S} - 3(\mathbf{S} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}] \quad (4.14)$$

$$\mathbf{B}_J(0) = -\frac{2\mu_B}{r^3} \left[\mathbf{L} - \frac{g_e}{2} (\mathbf{S} - 3(\mathbf{S} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}) \right]. \quad (4.15)$$

We need to evaluate

$$\langle \mathbf{J} \cdot \mathbf{B}_J \rangle = -\frac{2\mu_B}{r^3} [\ell(\ell+1) - S(S+1) + \langle 3(\mathbf{S} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} \cdot (\mathbf{L} + \mathbf{S}) \rangle] \quad (4.16)$$

Using $\langle (\mathbf{S} \cdot \hat{\mathbf{r}})^2 \rangle = \langle (\hat{\sigma} \cdot \hat{\mathbf{n}}/2)^2 \rangle = 1/4$, $\hat{\mathbf{r}} \cdot \mathbf{L} = 0$, and $S(S+1) = 3/4$, we obtain

$$\langle \mathbf{J} \cdot \mathbf{B}_J \rangle = -2\mu_B \langle \frac{1}{r^3} \rangle \ell(\ell+1) \quad (4.17)$$

So after all this work, the field turns out to depend only on ℓ . From Eq. 4.11, we obtain

$$ah = +\frac{g_e\mu_I\mu_B}{I} \langle \frac{1}{r^3} \rangle \frac{\ell(\ell+1)}{J(J+1)} \quad (4.18)$$

For a hydrogenic atom

$$\langle \frac{1}{r^3} \rangle = \frac{Z^3}{n^3} \frac{1}{\ell(\ell+1)(\ell+1/2)a_0^3} \quad (4.19)$$

Writing $\mu_I = g_I\mu_N I = g_I\mu_B(m_e/M_p)I$, we finally obtain

$$ah = \frac{g_e\mu_B Z^3 g_I \frac{m_e}{M_p}}{n^3 a_0^3} \frac{1}{(\ell+1/2)J(J+1)} \quad (4.20)$$

For hydrogen in the ground state, Eq. 4.20 gives

$$ah = \frac{4g_e}{3} hcR\alpha^2 g_I \frac{m_e}{M_p} \quad (4.21)$$

However, the argument has a flaw: $\langle 1/r^3 \rangle$ diverges for s -states. We must treat these states as a special case.

The orbital magnetic field is absent in s -states. However, the electron has finite probability of being at the origin and it must be regarded as a magnetic “cloud” with magnetization

$$\mathbf{M}(r) = \mu_e |\Psi(\mathbf{r})|^2 \quad (4.22)$$

The magnetization gives rise to a field at the origin

$$\mathbf{B}(0) = \mathbf{H}(0) + 4\pi\mathbf{M}(0) \quad (4.23)$$

The magnetization can be viewed as the sum of a small uniform sphere at the origin, plus a hollow sphere containing the remainder of the magnetization. It is easily shown that the field due to the hollow sphere vanishes. However, the uniform sphere give rise to a finite value of $\mathbf{H}(0)$ due to an equivalent surface magnetic charge density

$$\sigma_m = \mathbf{M}(0) \cdot \hat{\mathbf{n}} = \mathbf{M}(0) \cos \theta \quad (4.24)$$

which acts as the source of \mathbf{H} .

$$H_z(0) = - \int \frac{\sigma \cos \theta dS}{r^2} = -\frac{4\pi}{3} M(0). \quad (4.25)$$

Since $\mathbf{M}(0) = \mu_e |\psi(0)|^2 = -g_e \mu_B \mathbf{S} |\psi(0)|^2$,

$$\mathbf{B}(0) = -\frac{8\pi}{3} g_e \mu_B \mathbf{S} |\Psi(0)|^2 \quad (4.26)$$

which leads to the same result as Eq. 4.20. This s -state interaction is often called the “contact” (in the sense of touch) term.

We can summarize these results by combining Eqs. 4.15 and Eq. 4.26 taking $g_e = 2$:

$$\mathbf{B}(0) = -2\mu_B \left[\frac{\mathbf{L}}{r^3} - \frac{\mathbf{S}}{r^3} + \frac{3(\mathbf{S} \cdot \hat{r})\hat{r}}{r^3} - \frac{8}{3}\pi\delta(\mathbf{r})\mathbf{S} \right] \quad (4.27)$$

The first three terms in the bracket average to zero in an s -state; the last term contributes only in an s -state.

4.2.3 Hyperfine structure at zero magnetic field

The Hamiltonian at zero magnetic field is

$$H = ah \mathbf{I} \cdot \mathbf{J} \quad (4.28)$$

The total angular momentum is $\mathbf{F} = \mathbf{I} + \mathbf{J}$. In zero or low field, F and m_F are good quantum numbers. A “good” quantum number is the eigenvalue of an operator. At zero field, for instance, eigenfunctions of H are eigenfunctions of $\mathbf{F} = \mathbf{I} + \mathbf{J}$.

Physically, \mathbf{I} and \mathbf{J} are tightly coupled by the $ah\mathbf{I} \cdot \mathbf{J}$ interaction: they precess about each other, and about \mathbf{F} . Using $\mathbf{F}^2 = (\mathbf{I} + \mathbf{J})^2$, we obtain

$$\langle \mathbf{I} \cdot \mathbf{J} \rangle = [F(F+1) - J(J+1) - I(I+1)]/2 \quad (4.29)$$

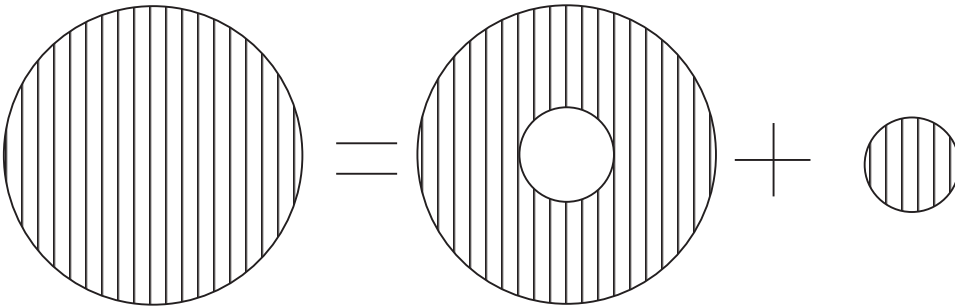


Figure 11. Decomposition of a spherically symmetric cloud of magnetization for finding the field at its center.

and for the energy levels

$$W(F, m) = \frac{ah}{2}[F(F+1) - J(J+1) - I(I+1)]. \quad (4.30)$$

Note that $m = \langle F_z \rangle$ remains a good quantum number at all fields. (The symbols F and I are used both for operators and eigenvalues: the meaning is clear from the context). F has values $|I - J|, |I - J + 1| \cdots |I + J|$. The interval between adjacent terms is

$$W(F) - W(F-1) = haF \quad (4.31)$$

This result, known as the Landé Interval Rule, played an important role in the early development of the theory of hyperfine structure. Furthermore, it is easy to show that

$$\sum_F (2F+1)W(F) = 0 \quad (4.32)$$

so that the “center of gravity” of a hyperfine multiplet is zero.

4.2.4 Electric quadrupole interaction

If the nucleus does not have a spherically symmetric charge distribution, it probably has a non-zero electric quadrupole moment

$$Q = \frac{1}{e} \int d^3r \rho(\mathbf{r}) [3z^2 - r^2] \quad (4.33)$$

which is < 0 for an oblate charge distribution. In contrast to the nuclear magnetic dipole, which is predominantly determined by the unpaired nucleons, Q is sensitive to collective deformations of the nucleus. Some nuclei are observed with 30% differences between polar and equatorial axes, so Q can be comparable to $\langle r^2 \rangle$, i.e. $\approx 10^{-24} \text{ cm}^2$.

The interaction energy of the quadrupole moment Q with the electron can be found by expanding the term $|\mathbf{r}_e - \mathbf{r}_N|^{-1}$ in spherical harmonics and evaluating the resulting expressions in terms of Clebsch-Gordon coefficients. The resulting energy shifts are then

$$E_{hf}^Q = BC(C+1) \quad (4.34)$$

where

$$B = \frac{3(Q/a_o^2)}{8I(2I-1)J(J+1)} < \frac{1}{r^3} > R_\infty \quad (4.35)$$

and

$$C = [F(F+1) - J(J+1) - I(I+1)] \quad (4.36)$$

[Note that $\mathbf{I} \cdot \mathbf{J}/\hbar^2$, which was involved in $H_{\text{mag}}^{\text{hf}}$, is equal to $C/2$].

The preceding expressions, like the corresponding ones for the magnetic interactions, have several significant omissions. The most important are relativistic corrections and core shielding corrections. Calculations of core shielding have been made by Sternheimer [2], and the quadrupole shielding by the core is sometimes prefixed by his name.

4.2.5 Order of magnitude of hyperfine structure

If one examines the magnetic hyperfine structure in Eq. 4.18, it is obviously quite similar to the expression for the fine structure expression in Chapter 3. The ratio is

$$\frac{E^{\text{mag}_{\text{hfs}}}}{E^{\text{fs}}} \approx g_I \left(\frac{m}{M_p} \right) \frac{1}{Z} \quad (4.37)$$

which is typically 10^{-3} to 10^{-4} . For a neutral atom, one can estimate

$$\frac{E_{\text{mag}}^{\text{hfs}}}{\hbar} = (\ell + 3/4)^{-3} \text{ GHz} \quad (4.38)$$

with a factor of 10 spread in either direction.

The quadrupole interaction is generally considerably smaller. An estimate is

$$B/\hbar \approx 0.01 Z(\ell + 1/2)^{-3} \text{ GHz} \quad (4.39)$$

Thus one generally expects that magnetic hyperfine structure dominates electric hyperfine structure in atoms. The opposite is generally true in molecules for two reasons: unpaired electrons are relatively rare, and the molecular binding mechanism can create large electric field gradients at the sites of the nuclei.

In concluding this discussion of hyperfine structure in atoms I would like to point out that the preceding formulae are, except in hydrogenic atoms, only approximations and never permit one to extract the nuclear dipole or quadrupole moment with the full accuracy of laser spectroscopy experiment—let alone R.F. spectroscopy experiments. Thus A and B in the combined hyperfine energy formula

$$E^{\text{hfs}} = E_{\text{mag}}^{\text{hfs}} + E_{\text{el}}^{\text{hfs}} = \frac{1}{2}AC + BC(C + 1)$$

(with C from Eq. 4.36) should be regarded primarily as empirical constants from the standpoint of atomic physics. Even if the problems of connecting A and B with the nuclear moments could be solved, the principal result would be better measurements of nuclear properties.

4.3 Isotope Effects

When comparing the spectral lines originating from atoms whose nuclei differ only in the number of neutrons (eg. different isotopes of the same element), effects due to the finite mass and volume of the nucleus become apparent. Even neglecting hyperfine structure (by taking the center of gravity of the observed splitting), the spectral lines of the different isotopes vary slightly in position—generally at the many parts per million level. The difference between the lines of the various isotopes is referred to as the isotope shift: it is observed to have both positive (heavier isotope has higher energy spacing) and negative values.

General speaking, light ($A < 40$) elements have positive frequency shift whereas heavy elements ($A > 60$) have negative shifts. This reflects the contribution of two distinct physical processes to the shift; the finite mass shift (almost

always positive), and the nuclear volume shift (almost always negative). These will be discussed separately.

4.3.1 Mass effect

The origin of the mass effect is obvious from the Bohr energy level formula

$$E_n = E_n^\circ \left(\frac{M}{m+M} \right) \approx E_n^\circ \left(1 - \frac{m}{M} \right) \quad (4.40)$$

where the term involving m/M comes from solving the two body electron-nucleus (of mass M) system using the relative coordinate and associated reduced mass. Obviously increasing M increases E_n .

In two (or more) electron atoms the situation becomes more complicated due to the relative motion of the electrons. It would, for example, be possible to arrange the electrons symmetrically on opposite sides of the nucleus in which case there would be zero isotope effect. The virial theorem assures us that the mean value of the kinetic energy equals the negative of the total energy, so if we treat the nuclear motion as a perturbation on a fixed nucleus solution, the mass effect will be:

$$\Delta E_{n,M} = \frac{-p^2}{2M} = -\frac{1}{2M} \left[\sum_i \mathbf{p}_i \right]^2 = -\frac{m}{M} \left[\underbrace{\frac{1}{2m} \sum p_i^2}_{\text{Normal Shift}} + \underbrace{\frac{1}{2m} \sum_{i \neq j} \mathbf{p}_i \cdot \mathbf{p}_j}_{\text{Specific Shift}} \right] \quad (4.41)$$

The first term is called the normal shift since (using the virial theorem again) it is

$$\Delta E_{n,M}^{\text{Normal}} = -\frac{m}{M} E_n^0 \quad (4.42)$$

The second term is called specific because it depends on the atom's quantum state. A discussion can be found in Sobel'man (pp. 224-6). $\Delta E^{\text{Specific}} = 0$ unless there are two or more valence electrons. For electronic configuration specified by quantum numbers n, s, ℓ , Sobel'man finds:

$$\Delta E_{ns,n'\ell}^{\text{specific}} = (1 - 2S) \frac{m}{M} \frac{3f_{ns,n'\ell}}{2} \hbar \omega_{n's',n\ell} \quad (4.43)$$

where $3f_{ns,n'\ell}$ is the oscillator strength (see Chapter ??). Thus the specific shift has opposite signs for $S = 1$ and $S = 0$ states—a reflection of the fact that the specific isotope shift is closely related to the exchange interaction. Eq. 4.43 also reflects the general result that $\Delta E^{\text{Specific}} = 0$ unless the two electrons are connected by an allowed dipole transition (otherwise f will vanish). Furthermore the specific isotope shift is of the same order of magnitude as the normal isotope shift: for $f > 2/3$, in fact, it can be larger (reversing the sign of the mass dependence of the isotope effect.)

The preceding discussion shows that the fractional energy shift of a level due to the mass of the nucleus decreases rapidly with increasing mass of the nucleus. The normal part of this shift has a variation in the fractional magnitude due to

a change ΔM in the mass of the isotope of

$$\frac{\Delta E_{n,M+\Delta M}^{\text{Normal}} - \Delta E_{n,M}^{\text{Normal}}}{E_n} = \left(\frac{m}{M + \Delta M} - \frac{m}{M} \right) = \frac{m}{M} \left(\frac{\Delta M}{M} \right) \quad (4.44)$$

which decreases as M^{-2} , reaching 10 parts per million for a nucleus with $A = 54$ (assuming $\Delta M = 1$).

4.3.2 Volume effect

Inside the nucleus, the electrostatic potential no longer behaves like Ze/r , but is reduced from this value. If the valence electron(s) penetrate significantly into this region (eg. for s electrons) then its energy will rise, relative to the value for a point nucleus, because of this reduced potential. Adding neutrons to the nucleus generally spreads out the charge distribution, causing a further rise in its energy. This reduction in the binding energy results in a decrease of the transition energy and therefore to a negative mass shift (assuming that the s state is the lower energy state involved in the transition).

For an s state, the density of the electron probability distribution at the nucleus is given by the semi-empirical Fermi-Segré formula [1]:

$$|\Psi_s(0)|^2 = \frac{Z_a^2 Z}{\pi a_0^2 n^{*3}} \left(1 + \left| \frac{\partial \delta_s}{\partial n} \right| \right) \quad (4.45)$$

where δ_s is the quantum defect and $Z_a e$ the charge of the atomic core. Combining this with a model of the nuclear charge cloud results (Sobel'man p. 229) in the

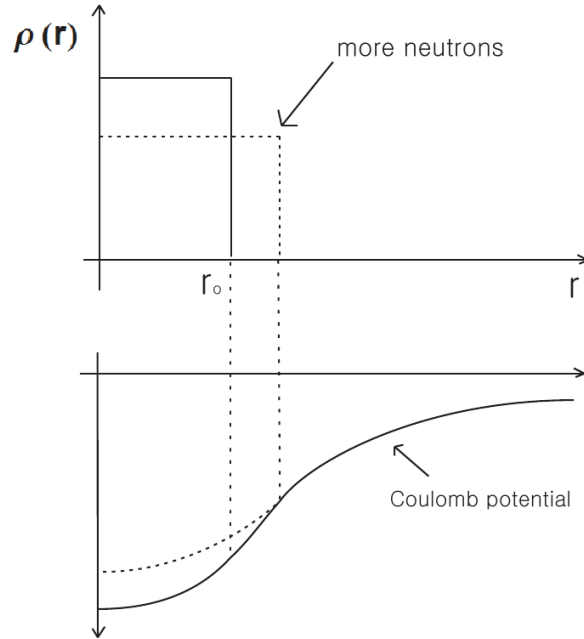


Figure 12. Simplified example of volume effect.

nuclear volume correction to the energy (of an s electron):

$$\Delta E_n^V = Z_a^2 \frac{R_\infty}{n^{*3}} \left(1 + \left| \frac{\partial \delta_s}{\partial n} \right| \right) C \quad (4.46)$$

with

$$C = \frac{4(\gamma + 1)}{[\Gamma(2\gamma + 1)]^2} B(\gamma) \left(\frac{2Zr_o}{a_o} \right)^{2\gamma} \frac{\delta r_o}{r_o} \quad (4.47)$$

where

$$\gamma = [1 - \alpha^2 Z^2]^{1/2} \quad (4.48)$$

Γ is the gamma function $\Gamma(N + 1) = N!$, $B(\gamma)$ is a factor which depends on the nuclear charge distribution. For a charged shell

$$B(\gamma) = (2\gamma + 1)^{-1} \quad (4.49)$$

and for a uniform charge

$$B(\gamma) = (2\gamma + 1)^{-1} \left(\frac{3}{2\gamma + 3} \right) \quad (4.50)$$

The nuclear radius is taken as (for atomic number A)

$$r_o = 1.15 \times 10^{-15} A^{1/3} m. \quad (4.51)$$

so that

$$\frac{\delta r_o}{r_o} = \frac{\delta A}{3A} \quad (4.52)$$

There are obviously a number of assumptions in these equations, and they should not be expected to work as well as expressions for the nuclear mass shift. Sobel'man states that the observed shift is generally 1/2 to 3/4 of the one given above except for non-spherical nuclei (eg. rare-earth nuclei) which have anomalously large shifts.

References

- [1] E.Fermi and E. Segré, *Memorie dell'Accademia d'Italia* **4**(Fisica), 131. An English translation is in Hindmarsh, Pergamon Press 1967, p. 259.
- [2] R.M. Sternheimer, *Phys. Rev.* **164**, 10(1967).