

Isotope shifts - Nuclear Mass and Size Effects on Atomic Structure

When we derived the solutions of the Dirac equation and their corresponding energies in the last lectures we implicitly assumed that the nucleus can be described as an infinitely heavy point charge. Both assumptions are well justified, however if we want to acquire a higher precision of our results we need a better approximation of the atomic system.

Nuclear Size Effect

From classical electrodynamics we know that a spherically symmetric charge distribution at distances larger than its radius generates the potential of a point charge. Inside of the distribution, however, the potential is different. The wavefunctions of s -orbitals especially extend all the way to the center of the nucleus and, thus, are affected by the non-coulombic potential at small radii. Consequently we have to formulate the nuclear potential as a function of two parameters (i) the radial coordinate r and (ii) a radial parameter R that is related to the mean square or charge radius R_{rms} of the nucleus

$$R_{rms} = \left(\frac{\int \rho_N(\mathbf{r}) r^2 d\mathbf{r}^3}{\int \rho_N(\mathbf{r}) d\mathbf{r}^3} \right)^{\frac{1}{2}}, \quad (1)$$

where $\rho_N(r)$ is the nuclear charge distribution.

To calculate the corrections to the relativistic energies by the nuclear size, we can use first order perturbation theory and calculate the expectation value of the potential difference due to a difference in the radial parameter R . We may write

$$\begin{aligned} \Delta E_i &= \langle \Delta V(r, R) \rangle_i \\ &= \langle V(r, R) - V(r, R + \Delta R) \rangle_i \\ &= \langle V(r, R) - V(r, R) - \partial_R V(r, R) \Delta R + \mathcal{O}(\Delta R^2) \rangle_i \\ &\approx - \langle \partial_R V(r, R) \rangle_i \Delta R \end{aligned} \quad (2)$$

where $\langle \cdot \rangle_i$ is the expectation value with respect to an electronic state described by a set of quantum numbers i .

The isotope shift caused by the nuclear size effect is called the *field shift* (FS), caused by the different nuclear charge radii of different isotopes with mass numbers A and A^0 .

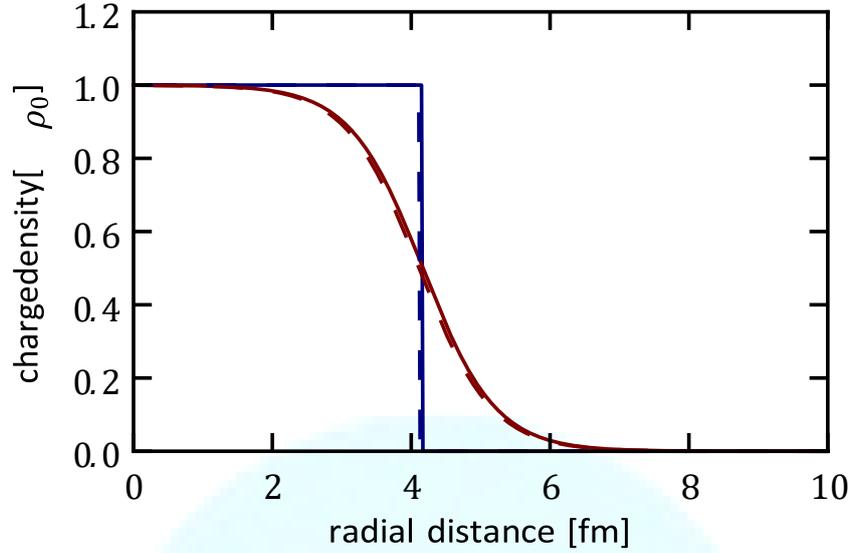


Figure 1: Nuclear charge Distribution for Iron ^{56}Fe and its second most abundant isotope ^{54}Fe showing both the Thomas Fermi model (6) (red lines) and the model of a uniformly charged sphere (5) (blue lines).

It is a lengthy derivation to show that the field shift can be parametrized as

$$\Delta E_{FS}^{AA'} = F (\Delta R_{rms})^2, \quad (3)$$

where we defined the *field shift constant* F . If we can write the Potential difference $\Delta V(r,R)$ as

$$\Delta V(r,R) = F(r,R)\Delta(R_{rms})^2 \quad (4)$$

the field shift constant may be calculated as the expectation value of $F(r,R)$.

There exists a variety of models to describe the charge distribution in a nucleus, the simplest of which is the uniformly charged sphere:

$$\rho(r, R) = \begin{cases} \rho_0 & \text{for } r < R \\ 0 & \text{for } r \geq R \end{cases} \quad (5)$$

A more accurate description of the nuclear charge density was devised by Thomas Fermi, smoothening the decrease of $\rho(r,R)$ towards larger radii.

$$\rho(r, R) = \frac{\rho_0}{1 + e^{\frac{r-R}{a}}}, \quad (6)$$

where R is the radius at which the charge density is fallen off by 50% and a a second parameter related to the width of the transition towards zero charge density. We notice that the type of charge distribution has only little influence on the nuclear size effect and, especially, on the isotope shift.

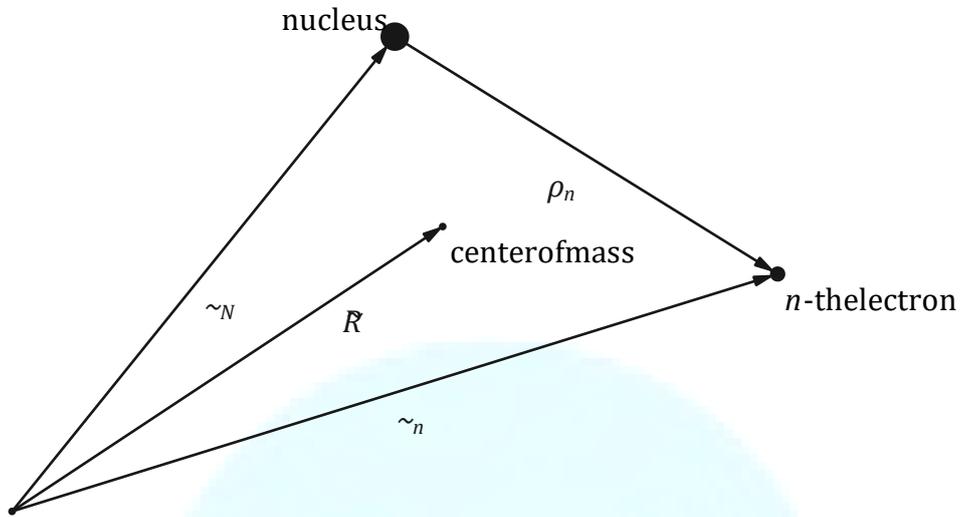


Figure 2: Partial sketch of the geometry of a N -electron atom and the correspondingly chosen relative center-of-mass coordinates ρ_i and R .

Kinetic isotope shifts

In addition to the effects that different nuclear charge distributions have on the electronic level energies, we still need to discuss the deviations caused by the nucleus not being infinitely heavy.

Let us consider the kinetic energy of a N -electron system with a nucleus with mass number A and resulting mass M_A in some inertial frame

$$\hat{T} = \frac{\hat{\mathbf{p}}_N^2}{2M_A} + \sum_{n=1}^N \frac{\hat{\mathbf{p}}_n^2}{2m_e} \tag{7}$$

As it can be recalled from non relativistic quantum mechanics the observer of an atom is at rest with respect to the center of mass (cms) frame of the atom. It is, however, an approximation to assume that the cms is in the center of the nucleus, it rather is at

$$= \frac{M_A \mathbf{r}_N + m_e \sum_{n=1}^N \mathbf{r}_n}{M_A + Nm} \tag{8}$$

where N is the number of electrons. If, in addition, we introduce the relative coordinate of the n -th electron

$$\rho_n = r_N - r_n \quad (9)$$

with the corresponding momenta P and π_n we obtain for the kinetic energy in the cms frame:

$$\hat{T}_{cms} = \frac{1}{2\mu} \sum_n \hat{\pi}_n^2 + \frac{1}{M_A} \sum_{n < k} \hat{\pi}_n \cdot \hat{\pi}_k + \frac{P^2}{2(M_A + Nm_e)} \quad (10)$$

where $\mu = \frac{m_e M_A}{m_e + M_A}$ is the reduced mass of the electron. The term proportional to P^2 is just a global shift due to the coordinate transformation and can be separated off. We will have a closer look on the other two terms below.

Normal mass shift

Let us investigate Eq. (10) term by term. The first term is the kinetic energy of the n -th electron, now expressed with respect to the reduced mass μ instead of the electron mass m_e . This is what we call the *normal mass shift* (NMS). To find the corresponding perturbation hamiltonian we write:

$$\begin{aligned} \frac{1}{2\mu} \sum_n \hat{\pi}_n^2 &= \frac{m_e + M_A}{2m_e M_A} \sum_n \hat{\pi}_n^2 \\ &= \frac{1}{2m_e} \sum_n \hat{\pi}_n^2 + \frac{1}{2M_A} \sum_n \hat{\pi}_n^2 \end{aligned} \quad (11)$$

The first term is the kinetic energy of the n -th electron in the rest frame of the nucleus. Thus the second term can be taken as a perturbation, that is approximately m_e/M_A smaller than the unperturbed kinetic energy:

$$\hat{H}_{NMS} = \frac{1}{2M_A} \sum_n \hat{\pi}_n^2 \quad (12)$$

This perturbation Hamiltonian is a correction to the kinetic energy, which occurs explicitly only in the non-relativistic Schrödinger equation. It is, however, plausible that the non-relativistic correction above resembles the leading order of the relativistic case. Thus we can use it, to a good approximation, for the calculation of the NMS correction.

The wave functions derived in the previous lecture were obtained for an infinitely heavy nucleus at rest in the origin. Thus \hat{H}_{NMS} corresponds to the kinetic energy operator T_∞ of such a system up to a prefactor of $\frac{M_A}{m_e}$. Thus we can write for the energy correction to an unperturbed state i :

$$\begin{aligned}
 \Delta E_i &= \frac{1}{2M_A} \left\langle \sum_n \hat{\pi}_n^2 \right\rangle_i \\
 &= \frac{m_e}{M_A} \frac{1}{2m_e} \left\langle \sum_n \hat{\pi}_n^2 \right\rangle_i \\
 &= \frac{m_e}{M_A} \left\langle \hat{T}_\infty \right\rangle_i
 \end{aligned} \tag{13}$$

The virial theorem tells us that, for a r^{-1} type potential, the expectation value of the kinetic energy equals the negative expectation value of the total energy. Thus the correction is:

$$\Delta E_{nj} = -\frac{m_e}{M_A} E_{nj} \tag{14}$$

or for the NMS between to isotopes A and A' :

$$\Delta E_{nj}^{A A'} = \left(\frac{m_e}{M_A} - \frac{m_e}{M_{A'}} \right) E_{nj} \tag{15}$$

As you may find out in the seminar, this correction gives us already surprisingly accurate energies for hydrogen-like systems.

Specific mass shift

While the normal mass shift is an effect, that can be observed in hydrogen-like ions, the specific mass shift is an effect only occurring in many-electron systems. The second sum in Eq. (10) shows a so-called mass-polarization term. This term does not occur in the rest frame of an infinitely heavy nucleus. The correction caused by this term is a lot harder to calculate than the previous ones. We will only give an idea here, how it can be achieved. We assume again that the expectation value of the (non-relativistic) specific mass shift (SMS) operator

$$\hat{T}_{SMS} = \frac{1}{M_A} \sum_{n < k} \hat{\pi}_n \cdot \hat{\pi}_k \tag{16}$$

gives us the leading order correction to the relativistic energies E_{nj} . Let us take a look at the expectation value of only one of the terms in the summation

$$\langle \hat{\pi}_n \cdot \hat{\pi}_k \rangle = \langle \gamma_{nj} \mu_n | \hat{\pi}_n | \gamma_{nj} \mu_n \rangle \langle \gamma_{kj} \mu_k | \hat{\pi}_k | \gamma_{kj} \mu_k \rangle \tag{17}$$

which can be split up into two matrix elements, because the $\hat{\pi}_n$ are single-particle operators. Let us now rewrite the momentum operator using

$$r \times l = r \times (r \times p) = (r \cdot p)r - r^2 p \quad (18)$$

and thus **ENTRI**

$$-i \sim \hat{C}^1 \hat{\rho}_n - \frac{\hat{1} \pi \hat{n}}{\rho_n} C \times \hat{l}, \quad (19)$$

where we introduced the rank-1 angular tensor operator $\hat{C}^1 = \frac{\hat{\rho}}{\rho}$. This operator is now separated into a radial and an angular part, which allows us to calculate the corresponding matrix elements (17) with the wave functions we already know.

Analysis of isotope shift experiments

If the isotope shift is measured in experiments it appears as a net effect and the different contributions (field shift, mass shifts) are not obviously separated. Thus let us combine the results of the previous sections to the total shift between two isotopes A and A^0 :

$$\begin{aligned} \Delta E_i^{AA'} &= \langle \hat{H}_{NMS} \rangle_i + \langle \hat{T}_{SMS} \rangle_i + F_i (\Delta R_{rms}^{AA'})^2 \\ &= \frac{M_{A'} - M_A}{M_A M_{A'}} K_i + F_i (\Delta R_{rms}^{AA'})^2, \end{aligned} \quad (20)$$

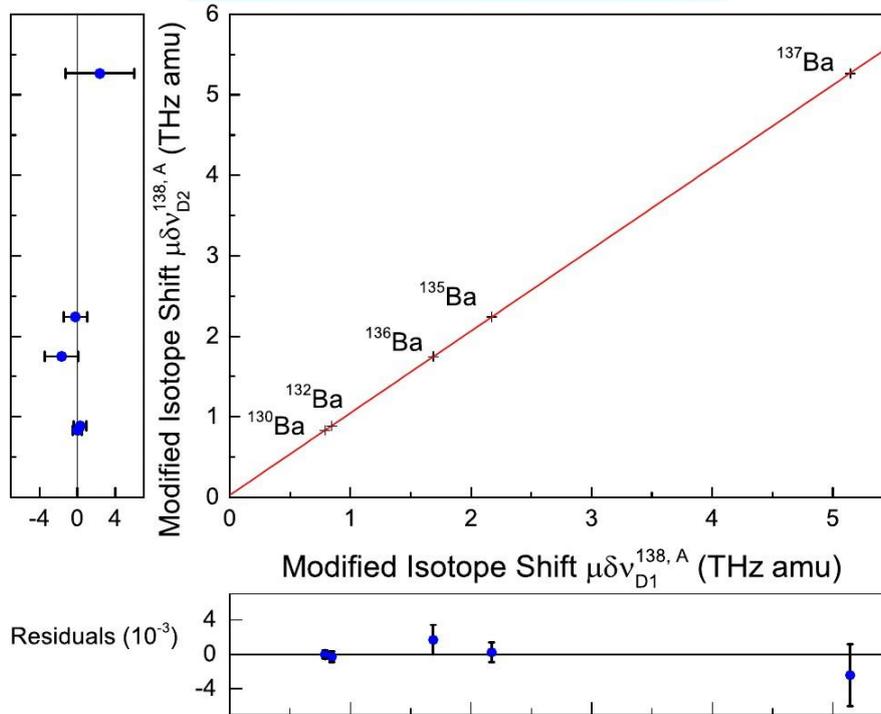


Figure 3: King plot of two transitions in Ba^+ . The transitions are $6s^2S_{1/2} \rightarrow 6p^2P_{1/2}$ (D1) and $6s^2S_{1/2} \rightarrow 6p^2P_{3/2}$ (D2).

where we hide all the messy expectation values of momentum operators in the *total mass shift parameter* K_i and only show the dependency on the masses of the isotopes in question. Note that sometimes the prefactor of K_i is expressed using dimensionless mass parameters in order to give K_i the dimension of energy.

Now, let us imagine an experiment, where the total isotope shift (20) is measured for a bunch of isotopes A_k with respect to a reference isotope A_{ref} . These values can be plotted as a function of M_{A_k} . The linearity of the resulting graph can be used as a measure for the quality of the data. The slope and the y -intercept of the line give us access to the mass and field shift parameters as well as the nuclear radii. This way of graphically analyzing experimental data is called *King plot analysis*.

There is another type of King plot worth considering. If we were to compare the isotope shift of two different states (or transitions) i and j we could rewrite Eq. (20) and get

$$\frac{M_A M_{A'}}{M_A - M_{A'}} \Delta E_i^{AA'} = \frac{F_i}{F_j} \frac{M_A M_{A'}}{M_A - M_{A'}} \Delta E_j^{AA'} + K_i - \frac{F_i}{F_j} K_j. \quad (21)$$

Introducing now the modified isotope shifts $\tilde{\Delta E}_i^{AA'} = \frac{M_A M_{A'}}{M_A + M_{A'}} \Delta E_i^{AA'}$ we get a line with slope F_i/F_j and y -intercept $K_i - K_j F_i/F_j$. Note that, if the isotope shifts are taken as experimental input, this equation is independent on the nuclear radius. Thus, the slope of the King plot line is an extremely stable quantity particularly useful for experiment-theory comparisons.

