Hyperfinecourse A: electric monopole shift

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Abstract

This document is meant for optional background reading when studying www.hyperfinecourse.org. It deals with one of the chapters of this course. The formal course content is defined by the website and videos. The present document does not belong to the formal course content. It covers the same topics, but usually with more mathematical background, more physical background and more examples. Feel free to use it, as long as it helps you mastering the course content in the videos. If you prefer studying from the videos only, this is perfectly fine.

The present text has been prepared by Jeffrey De Rycke (student in this course in the year 2018-2019). He started from a partial syllabus written by Stefaan Cottenier for an earlier version of this course, and cleaned, edited and elaborated upon that material. That syllabus was itself inspired by a course taught by Michel Rots at KU Leuven (roughly 1990-1995).

1 Monopole Shift

1.1 Interaction Energy Nucleus And Electrons

In the previous chapter, we have seen that we can Taylor-expand the interaction term between the nucleons and the electrons as follows:

$$\hat{Q} \otimes \hat{V} = \hat{Q}^{(0)} \otimes \hat{V}^{(0)} + \hat{Q}^{(1)} \otimes \hat{V}^{(1)} + \hat{Q}^{(2)} \otimes \hat{V}^{(2)} + \dots \quad (1)$$

With the following expressions:

$$Q_q^n = eZ\sqrt{\frac{4\pi}{2n+1}} \langle I| r_1^n Y_q^n (\theta_n, \phi_n) |I\rangle \quad (2)$$

$$V_q^n = -\frac{eN}{\sqrt{4\pi}\epsilon_0} \sqrt{\frac{1}{2n+1}} \left\langle \psi_e^{(0)} \right| \frac{1}{r_e^{n+1}} Y_q^n (\theta_e, \phi_e) \left| \psi_e^{(0)} \right\rangle \quad (3)$$

Where we made the agreement to treat all nuclear properties as phenomenological parameters, whilst keeping the electronic properties as operators. As well as keeping $r_e > r_n$. Suppose we now want to calculate the first term for a nucleus with one electron. We will get the following expressions:

$$Q_{00} = \frac{\sqrt{4\pi}}{\sqrt{4\pi}} \int \rho_n(\vec{r}) d\vec{r} = eZ \quad (4)$$

$$V_{00} = \frac{1}{4\pi\epsilon_0} \frac{\sqrt{4\pi}}{\sqrt{4\pi}} \int \frac{\rho_n(\vec{r})}{r} d\vec{r} = \frac{-e}{4\pi\epsilon_0} \langle \Psi_e| \frac{1}{r} |\Psi_e\rangle \quad (5)$$

$$E_0^0 = Q_{00} V_{00} = \frac{-e^2 Z}{4\pi\epsilon_0} \langle \Psi_e| \frac{1}{r} |\Psi_e\rangle \quad (6)$$

As you can see, these are just the non-relativistic energy levels of a point charge Ze in the potential of an electron.

Order	Multipole moment or field	First-order quasimoment or quasifield	Second-order quasimoment or quasifield	...
$O(0)$	MI:	$\mathrm{MS}^{(1)}$:	$\mathrm{MS}^{(2)}$:	...
	$M \propto r^0 Y_{00}$	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$	
	$V \propto v(0)$	$\tilde{V}^{(1)} \propto \Delta v(0)$	$\tilde{V}^{(2)} \propto \Delta^2 v(0)$	
$O(2)$	QI:	$\mathrm{QS}^{(1)}$:	$\mathrm{QS}^{(2)}$:	
	$Q \propto r^2 Y_{20}$	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$	...
	$V_{ij} \propto \partial_{ij} v(0)$	$\tilde{V}^{(1)}_{ij} \propto \partial_{ij} \Delta v(0)$	$\tilde{V}^{(2)}_{ij} \propto \partial_{ij} \Delta^2 v(0)$	
$O(4)$	HDI:	$\mathrm{HDS}^{(1)}$:	$\mathrm{HDS}^{(2)}$:	
	$H \propto r^4 Y_{40}$	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$	...
	$V_{ijkl} \propto \partial_{ijkl} v(0)$	$\tilde{V}^{(1)}_{ijkl} \propto \partial_{ijkl} \Delta v(0)$	$\tilde{V}^{(2)}_{ijkl} \propto \partial_{ijkl} \Delta^2 v(0)$	
...	...	...	...	...

Figure 1: *Systematic overview of nuclear multipole and quasi-multipole-moments and electric multipole and quasi-multipole-fields that appear in the multipole expansion of two interacting (and overlapping) classical charge distributions. The first column gives the regular multipole expansion for point nuclei: the monopole, quadrupole, and hexadecapole interactions. The next columns give the quasi-multipole-moments/fields for every multipole interaction, denoted by a tilde: these are corrections to the multipole interactions due to electron penetration into an extended nucleus. Entries in the large round brackets are by generalization only, and are not systematically derived in this course. The objects in each line are spherical tensors of a given rank (rank 0 for line 1, rank 2 for line 2, and rank 4 for line 3).*

A nucleus is, however, not a point charge. Further multipole moments can be calculated to further correct the energy levels due to the shape of the nucleus. In case of charge-charge interactions, these can be found via the quadrupole moment, the hexadecapole moment,... Not only does the shape of the nucleus amount to corrections, so does the fact that the nucleus and the electrons can overlap. In a fully exact description of the multipole expansion with overlapping charged distributions, every individual multipole term itself becomes a series expansion in powers of a quantity that is characteristic for the amount of overlap. Most of the effect of overlap is usually captured already in the first non-leading term of each of those expansions. The first order correction to the monopole moment is called the "first order monopole-shift" and will be the topic of this chapter. The first order correction to the quadrupole moment is called the "first order quadrupole shift", and so on and so forth. Each higher order moment having a smaller value then the previous one. The same goes for the order of the overlap correction. The second order monopole shift will be much smaller then the first order monopole shift.

1.2 First-order Monopole Shift Without Overlap

On the previous page, we have calculated the monopole correction due to the interaction between the nucleus and the electrons. The full energy level up to this correction (with N electrons) is as follows:

$$E_{sh}^{qq\,(0)} = E_I + \left\langle \psi_e^{(0)} \otimes I \right| \hat{T}_e + \hat{U}_{ee} - \frac{e^2 NZ}{4\pi\epsilon_0\, r_e} \left| I \otimes \psi_e^{(0)} \right\rangle \tag{7}$$

$$= \underbrace{E_I + E_e + E_{ee}}_{E_\alpha} - \frac{e^2 NZ}{4\pi\epsilon_0} \langle I|\, I\rangle \underbrace{\left\langle \psi_e^{(0)} \left| \frac{1}{r_e} \right| \psi^{(0)} \right\rangle}_{\left\langle \frac{1}{r_e} \right\rangle} \tag{8}$$

$$= E_\alpha - \frac{e^2 NZ}{4\pi\epsilon_0} \left\langle \frac{1}{r_e} \right\rangle \tag{9}$$

E_α is just shorthand notation for some contributions that will always be the same. In the second term we again have the (dot) product between the monopole moment of the nucleus eZ and the monopole field at the origin due to the electrons, $\frac{-eN}{4\pi\epsilon_0} \left\langle \frac{1}{r_e} \right\rangle$ (as usual, we either consider a neutral atom (N=Z) or one of the nuclei of a solid, with the origin chosen at that nucleus). Note that we again use the fact that we have no knowledge of the nuclear many-body wave function $|I\rangle$): instead of calculating the monopole moment from the nuclear many-body wave function, we replace it by the experimentally known total charge of the nucleus.

This shape-dependent monopole contribution of the charge-charge interaction, is by far the largest contribution to the electrostatic energy of the system nucleus + electrons. It is insensitive to details of the nuclear charge distribution, but through $< \frac{1}{r_e} >$ sensitive to details of the electronic charge distribution. Different states $|\psi_e^{(0)}>$ will lead to different $< \frac{1}{r_e} >$ and therefore to the distinct atomic levels with their eV-separation in the first zoomed in part of VIP-1.

1.3 First-order Monopole Shift With Overlap

Let us now look at the monopole term, with a first order correction due to overlap. Looking back at the gravitational result, the size-dependent monopole contribution is:

$$E_{sz}^{qq\,(0)} = \frac{eZ}{6} \begin{bmatrix} \langle r_n^2 \rangle & 0 & 0 \\ 0 & \langle r_n^2 \rangle & 0 \\ 0 & 0 & \langle r_n^2 \rangle \end{bmatrix} \cdot \begin{bmatrix} \frac{\Delta V(\vec{0})}{3} & 0 & 0 \\ 0 & \frac{\Delta V(\vec{0})}{3} & 0 \\ 0 & 0 & \frac{\Delta V_e(\vec{0})}{3} \end{bmatrix} \tag{10}$$

$$= \frac{eZ}{6}\, \Delta V(\vec{0})\, \underbrace{\langle I|\, r_n^2\, |I\rangle}_{\langle r_n^2 \rangle} \tag{11}$$

Using Poisson's equation:

$$\Delta V_e(\vec{r}_e) \quad = \quad -\frac{\rho_e(\vec{r}_e)}{\epsilon_0} \tag{12}$$

the energy including shape- and size-dependent monopole contributions becomes[1]:

$$E_{qq}^{(0)} \quad = \quad E_\alpha \, - \, \frac{e^2 N Z}{4\pi\epsilon_0} \left\langle \frac{1}{r_e} \right\rangle \, - \, \frac{eZ}{6\epsilon_0} \, \rho_e(\vec{0}) \, \left\langle r_n^2 \right\rangle \tag{13}$$

Note that the size-dependent contribution is always positive. Equation 13 can be rewritten as:

$$E_{qq}^{(0)} \quad = \quad E_\alpha \, + \, \tilde{\mathrm{Q}} \left\{ -\frac{eN}{4\pi\epsilon_0} \left\langle \frac{1}{r_e} \right\rangle \right\} \, + \, \tilde{\mathrm{Q}} \left\{ -\frac{1}{6\epsilon_0} \, \rho_e(\vec{0}) \, \left\langle r_n^2 \right\rangle \right\} \tag{14}$$

with $\tilde{\mathrm{Q}} = eZ$ the nuclear charge. This notation shows explicitly that both the shape- and size-dependent monopole contributions are a product between the nuclear charge (the nuclear monopole moment) and a potential at the nucleus. The potential that appears in the shape-dependent contribution depends entirely on properties of the electrons (it is the electronic monopole field). The effect of the overlap between nuclear and electronic charge distributions can be interpreted as due to an extra positive potential $-\frac{1}{6\epsilon_0} \, \rho_e(\vec{0}) \, \left\langle r_n^2 \right\rangle$ at the nucleus. This potential depends not only on the electronic property $\rho_e(\vec{0})$, but also on the nuclear property $\left\langle r_n^2 \right\rangle$. The latter is not really surprising. If electrons penetrate into the nucleus, they will interact differently with a nuclear charge that is contained into a small or a large volume. This difference is expressed by the mean square nuclear radius. In the limiting case of a point nucleus ($\left\langle r_n^2 \right\rangle \to 0$), this size-dependent correction becomes zero, as we intuitively expect. The same is true when electrons can/do not enter the nucleus. Then this term is zero as well.

1.4 Electrons Inside The Nucleus

We have said that the size-dependent monopole term arises from electrons penetrating the nucleus. The questions we now have to ask ourselves is: do electrons penetrate the nucleus? In other words, does this term even exist in reality? In a non-relativistic treatment, s-electrons do have a non-zero probability at the position of the nucleus $\vec{r} = \vec{0}$. This happens even if the nucleus is a single mathematical point, as the s-electron wave function does not vanish at $\vec{r} = \vec{0}$. In a relativistic treatment also the $p_{\frac{1}{2}}$ electrons (= relativistic quantum number $\kappa = 1$, from the Dirac equation) can penetrate into the nucleus. Can we estimate the size of said size-dependent term? Only[2] s-electrons will contribute to the overall charge density ρ_e at $\vec{0}$. For a fully filled s-shell, we can therefore write

[1] Check that all terms have dimensions of energy.

[2] in the non-relativistic treatment

$\rho_e(\vec{0}) = -2e \left|\psi_s(\vec{0})\right|^2$, where ψ_s is a (single particle) s-electron wave function. Filling out values for the Be-atom ($Z = 4$, $r_n = 1.4 \cdot 10^{-15} A^{\frac{1}{3}}$ m, $|\psi_{2s}(\vec{0})|^2 = \frac{2Z^3}{a_0^3 \pi}$) yields 3.5 μeV. Overlap corrections to the monopole term are therefore of the order of magnitude of μeV. In order to calculate numerical values for these corrections, experimental values for $\langle r_n^2 \rangle$ must be known (they cannot yet be calculated from first principles nuclear theory). Alternatively, if energies are measured, this equation can be used to determine $\langle r_n^2 \rangle$.

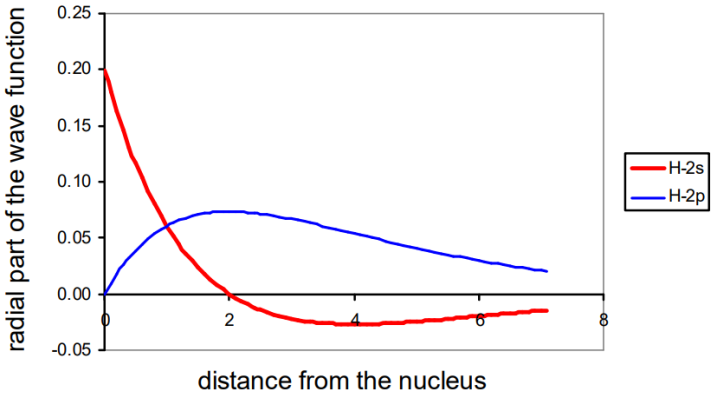

Figure 2: *Difference between radial part of the wave function for 2s and 2p electrons of the H-atom. One can cleary see that the 2s electrons have a change >0 to be at the origin.*

1.5 Isotope and Isomer Shift

The correction to the monopole energy due to the penetration of electrons into the nucleus does not lift any degeneracy, but only shifts the levels by a positive amount which depends on the amount of penetration and the mean square radius of the nucleus. The nuclei of different isotopes of the same element can be expected to have different nuclear radii, and hence different corrections. This effect is well-known in atomic spectroscopy as one of the contributions to the *isotope shift*, namely the *field shift*. There is another contribution to this isotope shift, which is due to the fact that different isotopes can have different masses: the *mass shift*. The observed isotope shift (in Fig. 2 on the next page) is the sum of field shift and mass shift. Two states (isomers, excited nuclei) of the same nucleus can have different radii a well, this is called the isomer shift. To be clear, this is not illustrated in Fig. 2.

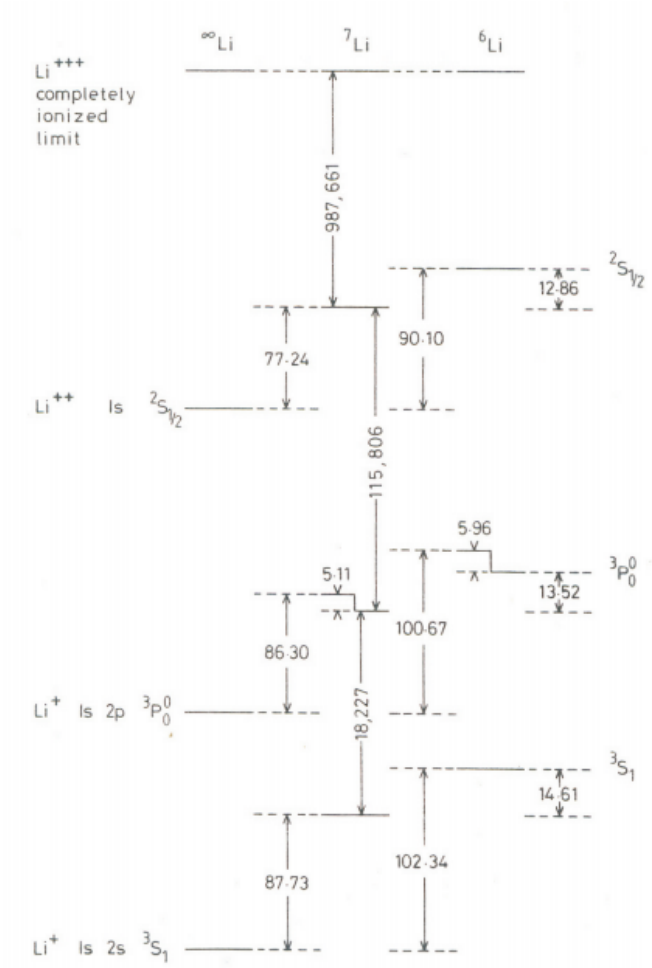

Figure 3: *Calculated mass shifts in free Li ions. All energies are relative to the completely ionized limit. Energies are expressed in* cm^{-1} *(multiply by 0.5809 to get values in* μeV*). For instance, the* $^3S_1$ *configuration (*$1s^1$ $2s^1$ *with the two spins parallel) in infinitely heavy* Li^+ *has an energy which is 87.73* cm^{-1} *(50.96* μeV*) lower than the same configuration in* $^7Li^+$*, and 102.34* cm^{-1} *(59.44* μeV*) lower than in* $^6Li^+$*. Comparisons with an infinitely heavy ion cannot be checked experimentally, but the difference of 14.61* cm^{-1} *(8.48* μeV*) between the* $^3S_1$ *configurations of* $^7Li^+$ *and* $^6Li^+$ *is present in experiments. Similar interpretations can be made for the* $^2S_{1/2}$ *configuration, while the* $^3P_0$ *configuration contains complications not discussed in this text. (Picture taken from* Isotope Shifts in Atomic Spectra*, W. H. King, Plenum Press, 1984.)*

1.6 Second Order Monopole Shift

We have just discussed the first order monopole shift, but what about the second order monopole shift? This correction is, as previously stated, much smaller then the first order shift (4^{th} power of nuclear radius instead of 2^{nd}). It will nonetheless pop up when dealing with so called "muonic atoms". These are atoms where one of the electrons is replaced by a muon, which is about 207 times heavier than the electron. Therefore it will circle much closer to the nucleus and have a larger overlap with said nucleus.

2 A Toy Model For The Monopole Shift

The writer of this document didn't think there was more background to add in addition to the course video about this topic. Writing about what is discussed in the video would be a literal translation from video to text, and this is not the purpose of these documents. For additional background on this video, please read https://biblio.ugent.be/publication/2988716/file/2988720.pdf. This is the paper from where said toy model originates and is writen by K. Rose and S. Cottenier (the lecturer of this course). The paper is free to download for everybody with a UGent account.