Many-Body Calculations of the Isotope Shift

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1 Introduction

Atomic energy levels are commonly evaluated assuming that the nuclear mass is infinite. In this report, we consider corrections to atomic levels associated with finite nuclear mass. These corrections are referred to as *isotope shifts*. We evaluate isotope shifts using many-body perturbation theory (MBPT), following the pioneering work by Mårtensson-Pendrill *et al.* [1, 2, 3, 4, 5, 6, 7, 8, 9]. We first give a brief discussion of contributions to the isotope shift, then go on to specific examples. For simplicity, the examples discussed here are limited to isotope shifts in atoms with a single valence electron.

We consider a nonrelativistic atom with N electrons of mass m_e at $(\vec{r}_1, \vec{r}_2, \cdots)$ and a nucleus of mass M_A at $\vec{r}_0$. The Hamiltonian for the $N+1$ particle atom may be written

$$H(\vec{r}_0, \vec{r}_1, \vec{r}_2, \cdots, \vec{p}_0, \vec{p}_1, \vec{p}_2, \cdots) = \frac{p_0^2}{2M_A} + \sum_i \frac{p_i^2}{2m_e} + \sum_i V_{e-N}(\vec{r}_i - \vec{r}_0) + \frac{1}{2}\sum_{i\neq j} V_{e-e}(\vec{r}_i - \vec{r}_j)\,. \tag{1}$$

Let us transform to relative coordinates:

$$\vec{\rho}_i = \vec{r}_i - \vec{r}_0 \tag{2}$$

$$\vec{R} = \frac{M_A\ \vec{r_0} + m_e \sum_i \vec{r}_i}{M_T}\,, \tag{3}$$

where $M_T = M_A + N\,m_e$. The generalized momenta conjugate to $\vec{\rho}_i$ and $\vec{R}$ are:

$$\vec{\pi}_i = \frac{1}{i}\vec{\nabla}_{\rho_i} \tag{4}$$

$$\vec{P} = \frac{1}{i}\vec{\nabla}_R \tag{5}$$

We find using the four previous equations:

$$\vec{p}_i = \vec{\pi}_i + \frac{m_e}{M_T}\vec{P} \tag{6}$$

$$\vec{p}_0 = -\sum_i \vec{\pi}_i + \frac{M_A}{M_T}\vec{P} \tag{7}$$

The kinetic energy term in the original Hamiltonian can be rewritten

$$\begin{aligned}
\text{K. E.} &= \frac{1}{2m_e}\left[\sum_i \pi_i^2 + 2\frac{m_e}{M_T}\sum_i \vec{\pi}_i\cdot\vec{P} + \frac{Nm_e^2}{M_T^2}P^2\right] \\
&+ \frac{1}{2M_A}\left[\left(\sum_i \vec{\pi}_i\right)^2 - 2\frac{M_A}{M_T}\sum_i \vec{\pi}_i\cdot\vec{P} + \frac{M_A^2}{M_T^2}P^2\right] \\
&= \frac{m_e+M_A}{2\,m_e\,M_A}\sum_i \pi_i^2 + \frac{1}{M_A}\sum_{i\neq j}\vec{\pi}_i\cdot\vec{\pi}_j + \frac{1}{2M_T}P^2 \qquad (8)
\end{aligned}$$

The wave function for the atom is therefore factorizable into a product of plane wave describing the center of mass motion and an N-electron wave function describing the motion relative to the nucleus. The Hamiltonian for the relative motion is

$$\begin{aligned}
H(\vec{\rho}_1,\vec{\rho}_2,\cdots,\vec{\pi}_1,\vec{\pi}_2,\cdots) &= \sum_i \frac{\pi_i^2}{2\,\mu} + \sum_i V_{e-N}(\vec{\rho}_i) + \frac{1}{2}\sum_{i\neq j} V_{e-e}(\vec{\rho}_i-\vec{\rho}_j) \\
&+ \frac{1}{M_A}\sum_{i\neq j}\vec{\pi}_i\cdot\vec{\pi}_j\,. \qquad (9)
\end{aligned}$$

where the reduced mass μ is given by

$$\mu = \frac{M_A\,m_e}{M_A+m_e}\,. \qquad (10)$$

1.1 Normal and Specific Mass Shifts

We write the Hamiltonian as a sum

$$\begin{aligned}
H(\vec{\rho}_1,\vec{\rho}_2,\cdots,\vec{\pi}_1,\vec{\pi}_2,\cdots) &= H_\mu + \Delta H \qquad (11) \\
H_\mu(\vec{\rho}_1,\vec{\rho}_2,\cdots,\vec{\pi}_1,\vec{\pi}_2,\cdots) &= \sum_i \frac{\pi_i^2}{2\,\mu} + \sum_i V_{e-N}(\vec{\rho}_i) \\
&+ \frac{1}{2}\sum_{i\neq j} V_{e-e}(\vec{\rho}_i-\vec{\rho}_j) \qquad (12) \\
\Delta H(\vec{\pi}_1,\vec{\pi}_2,\cdots) &= \frac{1}{M_A}\sum_{i\neq j}\vec{\pi}_i\cdot\vec{\pi}_j\,. \qquad (13)
\end{aligned}$$

Normal Mass Shift The effect of the finite nuclear mass on the first term is to scale the infinite mass Rydberg constant by the ratio $\mu/m_e = M_A/(M_A+m_e)$. The corresponding shift of the energy from the infinite-mass value is is referred to as the *normal mass shift*. The value of the normal mass shift is

$$\delta E_{\rm NMS} = E_\mu - E_{m_e} = \left(\frac{M_A}{M_A+m_e}-1\right)E_{m_e} = -\frac{m_e}{M_A+m_e}\,E_{m_e} \equiv -\frac{m_e}{M_A}\,E_\mu\,. \qquad (14)$$

Here E_{m_e} is the value of the energy in atomic units (calculated with the infinite-mass Rydberg constant). We may use the above expression with E_μ replaced by the experimental energy to evaluate the normal mass shift to obtain an accurate approximation to the normal mass shift.

Specific Mass Shift The correction to the energy from ΔH is referred to as the *specific mass shift*. The value of the specific mass shift is

$$\delta E_{\mathrm{SMS}} = \frac{1}{M_A} \left\langle \sum_{i \neq j} \vec{\pi}_i \cdot \vec{\pi}_j \right\rangle . \tag{15}$$

The energy is proportional to the mass (μ for H_μ) or (m_e for H_{m_e}) in the denominator of the kinetic energy. It follows that lengths scale inversely with mass and that kinetic energy scales directly as mass. The scaling of kinetic energy implies that momentum scales directly with mass. With the aid of these scaling relations, one may rewrite

$$\delta E_{\mathrm{SMS}} = \frac{M_A}{(M_A + m_e)^2} \left\langle \sum_{i \neq j} \vec{p}_i \cdot \vec{p}_j \right\rangle , \tag{16}$$

in the center of mass system. The scaling is required since we evaluate the SMS matrix element using infinite nuclear mass wave functions. The prescription is as follows:

(a) Express all answers in terms of the R_∞, the infinite mass Rydberg constant.

(b) Multiply the total energy by $-m_e/(M_A + m_e)$ to obtain the the normal mass shift.

(c) Multiply the matrix element of $\sum \vec{p}_i \cdot \vec{p}_j$ by $M_A/(M_A + m_e)^2$ to find the spectfic mass shift.

Alternatively, we may use experimental energies for E_μ and evaluate the normal mass shift as

$$\delta E_{\mathrm{NMS}} = -\frac{m_e}{M_A} E_{\mathrm{expt}} . \tag{17}$$

1.2 Field Shift

In addition to the normal and specific mass shifts, we have an additional shift from the change in nuclear size as we shift from one isotope to the next. This shift is referred to as the field shift and is parameterized as

$$\delta E = -F \delta \left\langle r^2 \right\rangle , \tag{18}$$

where $\delta \left\langle r^2 \right\rangle$ is the change in the root-mean-square radius if the nucleus. Assuming that the nucleus can be described as a uniformly charged ball of radius

R, the nuclear potential is

$$V(r,R) = \begin{cases} -(Z/2R)\ \left[3 - r^2/R^2\right]\,, & r < R \\ -Z/r\,, & r \geq R \end{cases} \tag{19}$$

The change in $V(r,R)$ induced by a change δR in the radius is

$$\delta V = \frac{3Z}{2R^2}\left[1 - \frac{r^2}{R^2}\right]\delta R, \quad r \leq R\,. \tag{20}$$

Using the the fact that $\left\langle r^2 \right\rangle = 3R^2/5$ for a uniform distribution, one may rewrite the above equation in the form

$$\delta V = \frac{5Z}{4R^3}\left[1 - \frac{r^2}{R^2}\right]\delta\left\langle r^2 \right\rangle, \quad r \leq R\,. \tag{21}$$

With this result in mind, we can introduce the single-particle operator $h_{\rm nuc}(r)$

$$h_{\rm nuc} = -\frac{5Z}{4R^3}\left[1 - \frac{r^2}{R^2}\right], \quad r \leq R \tag{22}$$

and find the field-shift parameter as

$$F = \langle h_{\rm nuc} \rangle\,. \tag{23}$$

2 MBPT Calculations of SMS

The operator

$$T = \sum_{i \neq j} \vec{p}_i \cdot \vec{p}_j$$

can be expressed in second quantization as the sum of one- and two-particle operators

$$\frac{1}{2}\sum_{ijkl} t_{ijkl}\, :a_i^\dagger a_j^\dagger a_l a_k: + \sum_{ij} t_{ij}\, :a_i^\dagger a_j:\,,$$

where

$$t_{ijkl} = \langle ij|\, \vec{p}_1 \cdot \vec{p}_2\, |kl\rangle \tag{24}$$

$$t_{ij} = \sum_a \langle ai|\, \vec{p}_1 \cdot \vec{p}_2\, |aj\rangle - \sum_a \langle ai|\, \vec{p}_1 \cdot \vec{p}_2\, |ja\rangle\,. \tag{25}$$

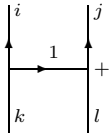
The "direct" part of the one-particle operator t_{ij} vanishes by reasons of symmetry.

2.1 Angular Decomposition

The two-particle operator t_{ijkl} may be decomposed in an angular-momentum basis as

$$t_{ijkl} = \sum_{\lambda} (-1)^{\lambda} \langle i|\, p_{\lambda}\, |k\rangle \langle j|\, p_{-\lambda}\, |l\rangle\,, \tag{26}$$

which, in turn, can be expressed diagramatically as

$t_{ijkl} = -$  $+ \quad T_1(ijkl)\,,$ (27)

where

$$T_1(ijkl) = -\langle i||C^1||k\rangle\, \langle j||C^1||l\rangle\, P(ac)\, P(bd)\,. \tag{28}$$

In Eq. (28), the quantities $P(ik)$ are radial matrix elements of the momentum operator. We give explicit forms for these reduced matrix elements in the following subsection.

2.2 Matrix elements of momentum

Let us digress to give explicit forms for the matrix elements of the momentum operator. We first consider the nonrelativistic case.

2.2.1 Nonrelativistic case:

We write $\vec{p} = \frac{1}{i}\vec{\nabla}$ and note that in the nonrelativistic case

$$\begin{aligned}
\langle b|\vec{\nabla}|a\rangle &= \int d^3r\, \frac{1}{r} P_b(r)\, Y^{\star}_{l_b m_b} \vec{\nabla} \left(\frac{1}{r} P_a(r)\, Y_{l_a m_a} \right) \\
&= \int_0^{\infty} dr\, P_b(r) \left(\frac{dP_a}{dr} - \frac{1}{r} P_a(r) \right) \int d\Omega\; Y^{\star}_{l_b m_b} \hat{r}\, Y_{l_a m_a} \\
&+ \int_0^{\infty} dr\, P_b(r) P_a(r) \int d\Omega\; Y^{\star}_{l_b m_b} \vec{\nabla}\, Y_{l_a m_a}
\end{aligned} \tag{29}$$

Note that we can rewrite the operators on spherical harmonics in terms of vector spherical harmonics as

$$\hat{r} Y_{lm}(\hat{r}) = \vec{Y}^{(-1)}_{lm}(\hat{r}) \tag{30}$$

$$\vec{\nabla} Y_{lm}(\hat{r}) = \frac{\sqrt{l(l+1)}}{r}\, \vec{Y}^{(1)}_{lm}(\hat{r}) \tag{31}$$

Using the expansion of vector spherical harmonics in terms of $\vec{Y}_{JLM}(\hat{r})$, we easily establish that

$$\langle l_b m_b|\vec{\nabla}|l_a m_a\rangle = \begin{cases} (l_a+1)\langle l_b m_b|\hat{r}|l_a m_a\rangle & \text{for } l_b = l_a - 1, \\ -l_a \langle l_b m_b|\hat{r}|l_a m_a\rangle & \text{for } l_b = l_a + 1\,. \end{cases} \tag{32}$$

With the aid of this expression, We find

$$\langle b|\vec{\nabla}|a\rangle = \langle l_b m_b|\hat{r}|l_a m_a\rangle \int_0^\infty dr P_b(r)\left(\frac{dP_a}{dr} + \frac{l_a}{r}P_a\right), \quad l_b = l_a - 1, \tag{33}$$

and

$$\langle b|\vec{\nabla}|a\rangle = \langle l_b m_b|\hat{r}|l_a m_a\rangle \int_0^\infty dr P_b(r)\left(\frac{dP_a}{dr} - \frac{l_a+1}{r}P_a\right), \quad l_b = l_a + 1. \tag{34}$$

We may therefore write, as in Eq. (28),

$$\langle b|p_\lambda|a\rangle = \langle l_b m_b|\, C^1_\lambda\, |l_a m_a\rangle\ P(ba),$$

where the radial matrix element $P(ab)$ is

$$\begin{aligned} P(ba) &= \frac{1}{i}\int_0^\infty dr P_b(r)\left(\frac{dP_a}{dr} + \frac{l_a}{r}P_a\right), \quad l_b = l_a - 1, \\ &= \frac{1}{i}\int_0^\infty dr P_b(r)\left(\frac{dP_a}{dr} - \frac{l_a+1}{r}P_a\right), \quad l_b = l_a + 1. \end{aligned} \tag{35}$$

2.2.2 Relativistic case I:

It is simple to generalize the previous nonrelatvistic matrix element to the relativistic case. We may write

$$\langle b|p_\lambda|a\rangle = \langle \kappa_b m_b|\, C^1_\lambda\, |\kappa_a m_a\rangle\ P(ba),$$

where the relativistic radial matrix elements $P(ab)$ is

$$P(ba) = \frac{1}{i}\int_0^\infty dr\left[G_b(r)\left(\frac{dG_a}{dr} + \frac{\eta_a}{r}G_a\right) + F_b(r)\left(\frac{dF_a}{dr} + \frac{\zeta_a}{r}F_a\right)\right], \tag{36}$$

with $\eta_a = l_a$ or $-l_a - 1$, for $l_b = l_a - 1$ or $l_b = l_a + 1$, respectively; and $\zeta_a = l'_a$ or $-l'_a - 1$ for $l'_b = l'_a - 1$ or $l'_b = l'_a + 1$, respectively. Here $l' = l(-\kappa)$. This is the proper form for the matrix element of the momentum operator.

2.2.3 Relativistic case II:

An alternative form that is equivalent to the above in the nonrelativistic limit is obtained by replacing $\vec{p} \to m_e c\,\vec{\alpha}$. This form leads to

$$\begin{aligned} \langle b|p_\lambda|a\rangle = -im_e c\int_0^\infty dr\Big[&G_b(r)\,F_a(r)\ \langle \kappa_b m_b|\sigma_\lambda|-\kappa_a m_a\rangle \\ &-F_b(r)\,G_a(r)\ \langle -\kappa_b m_b|\sigma_\lambda|\kappa_a m_a\rangle\Big]. \end{aligned} \tag{37}$$

With the aid of the identity

$$\langle \kappa_b m_b|\sigma_\lambda|\kappa_a m_a\rangle = (\kappa_b + \kappa_a - 1)\langle \kappa_b m_b|C^1_\lambda|\kappa_a m_a\rangle\,, \tag{38}$$

we may write the matrix element in Eq. (37) as

$$\langle b|p_\lambda|a\rangle = -im_e c\ \langle\kappa_b m_b|C^1_\lambda|\kappa_a m_a\rangle \int_0^\infty dr\big[(\kappa_b-\kappa_a-1)G_b(r)\,F_a(r) + (\kappa_b-\kappa_a+1)F_b(r)\,G_a(r)\big]\,. \quad (39)$$

From this expression, one obtains the alternative expression

$$P(ba) = -i\,m_e c\int_0^\infty dr\big[(\kappa_b-\kappa_a-1)G_b(r)\,F_a(r)+(\kappa_b-\kappa_a+1)F_b(r)\,G_a(r)\big]\,. \quad (40)$$

for the radial integral of the momentum operator. In the Pauli approximation, we may replace

$$F_a(r) \to -\frac{1}{2m_e c}\left(\frac{dG_a}{dr}+\frac{\kappa_a}{r}G_a\right)\,,$$

leading to

$$\begin{aligned} P(ba) &= \frac{i}{2}\int_0^\infty dr\left[(\kappa_b-\kappa_a-1)\,G_b(r)\left(\frac{dG_a}{dr}+\frac{\kappa_a}{r}G_a\right)\right. \\ &\qquad \left. +\,(\kappa_b-\kappa_a+1)\,G_a(r)\left(\frac{dG_b}{dr}+\frac{\kappa_b}{r}G_b\right)\right] \\ &= \frac{1}{i}\int_0^\infty dr\ G_b(r)\left(\frac{dG_a}{dr}-\frac{(\kappa_b-\kappa_a)(\kappa_b+\kappa_a+1)}{2r}G_a\right)\,. \end{aligned} \quad (41)$$

By enumerating the six possible combinations, one can show that

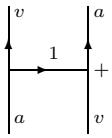
$$-\frac{(\kappa_b-\kappa_a)(\kappa_b+\kappa_a+1)}{2r} = \begin{cases} \frac{l_a}{r} & l_b = l_a-1 \\ -\frac{l_a+1}{r} & l_b = l_a+1 \end{cases}\,, \quad (42)$$

which is just the nonrelativistic expression for the radial matrix element. We will use Eq. (40) in our calculations because of its relative simplicity.

2.3 Lowest-order calculation

Consider an atom with a single valence electron described by an HF wave function. The lowest-order matrix element of T in a state v is given by

$$\langle v|T|v\rangle^{(1)} = t_{vv} = -\sum_a t_{vaav} = -\sum_a -$$



$$+\quad T_1(vaav)\,.$$

We can carry out the sum over magnetic substates using standard graphical rules to find:

$$\langle v|T|v\rangle^{(1)} = -\sum_a \frac{1}{[v]}\,|\langle v||C^1||a\rangle|^2\,|P(va)|^2\,. \quad (43)$$

where we have used the fact that

$$P(ba) = P(ab)^\star\,.$$

Table 1: Lowest-order matrix elements of the specific-mass-shift operator T for valence states of Li and Na.

Lithium $Z = 3$			Sodium $Z = 3$		
State	$E_{\rm HF}$	$\langle v\|T\|v\rangle$	State	$E_{\rm HF}$	$\langle v\|T\|v\rangle$
$2s$	-0.19632	0.00000	$3s$	-0.18203	-0.06150
$2p_{1/2}$	-0.12864	-0.04162	$3p_{1/2}$	-0.10949	-0.03201
$2p_{3/2}$	-0.12864	-0.04162	$3p_{3/2}$	-0.10942	-0.03199

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