The "Isomer" Shift

How much does the small but finite size of the atomic nucleus affect the total energy of the nucleus-plus-electrons atom?

In Mössbauer spectroscopy we are sensitive to the Coulombic energy shift due to the local electron density interacting with the extended nuclear charge.

- "point" nucleus plus atomic electrons

\[ H \Psi_e(r) = E \Psi_e(r) \] (1)

Electron wavefunction when the nucleus is treated as "point-like" Coulombic piece of the system energy Hamiltonian of the whole chemical system of the material, including molecular structure effects, to which \( H \Psi_e \) is a solution.

Treat the finite size of the nucleus as a 1st order time-independent perturbation. The procedure for computing the shift in system energy due to the slightly different potential function is

\[ \delta E_e = \langle \Psi_e | H_{\text{int}} | \Psi_e \rangle \] (2)

\[ \text{perturbing Hamiltonian due to finite size} \]

\[ \delta E_e \text{ in state energy relative to unperturbed case} = e (V(r) - V_o(r)) \text{ see next page} \]

\[ = \int \Psi_e^*(r) H_{\text{int}} \Psi_e(r) d^3r \] (3)

\[ \text{shift in state energy} = \text{point charge potential} \]

\[ \text{finite size potential} \]

\[ \text{assume spherical symmetry} \]

\[ = 4\pi \int r^2 d^3r \]

The interaction is particularly simple, involving no derivatives, so we can write

\[ \delta E_e = 4\pi e \int \Psi_e^*(r) \Psi_e(r) (V(r) - V_o(r)) r^2 d^3r \] (4)

\[ \Psi_e(r) \text{ electron density within the nucleus} \]

The potential \( V(r) \) differs from \( V_o(r) \) only inside the nucleus itself, so the integral only ranges over the nuclear size.
We assume the electronic wavefunction $\Psi_e(r)$ changes very little over the size of the nucleus, so we approximate

$$\Psi_e(r \gg R) \approx \Psi_e(0)$$  \hspace{1cm} (5)

and therefore factor this out of the integral $\Psi_e^*(r) \Psi_e(r) = \rho_e(0)$

$$\Delta E = 4\pi e_0 \rho_e(0) \int_0^R (V - V_0) r^2 \, dr$$  \hspace{1cm} (6)

$V_0$ is the Coulomb potential of a point-like nucleus, to which $\Psi_e(r)$ is the solution to the unperturbed Schrödinger equation:

$$V_0(r) = \frac{1}{4\pi e_0} \frac{2e}{r}, \quad r > 0$$  \hspace{1cm} (7)

$V(r)$ is the potential of a uniformly charged sphere, which is our model of the (positive) nuclear charge distribution. Let

$$\rho_n(r < R) = \frac{2e}{4\pi R^3} = \text{constant}$$  \hspace{1cm} (8)

be the charge distribution, then from Gauss's Law

$$\oint E(\hat{r}) \cdot d\vec{A} = \frac{1}{\varepsilon_0} \int \rho_n(r) \, dV$$  \hspace{1cm} (9)

leads to

$$E(\hat{r}) = \begin{cases} \frac{2e}{4\pi e_0} \frac{1}{r^2} & r < R \\ \frac{2e}{4\pi e_0} \frac{1}{R^2} & r > R \end{cases}$$  \hspace{1cm} (10)

quadratic rise of potential for $r < R$

Coulombic fall-off of potential for $r > R$

$$V(r) = -\int_r^R E(\hat{r}) \, d\hat{r} + V(R)$$  \hspace{1cm} (11)

$$= -\frac{2e}{4\pi e_0} \frac{1}{R^3} \int_r^R r^2 \, dr + \frac{2e}{4\pi e_0} \frac{1}{R}$$

$$= \frac{2e}{4\pi e_0} \left( \frac{1}{R^3} \left( \frac{1}{2} R^2 - \frac{1}{2} r^2 \right) + \frac{1}{R} \right)$$  \hspace{1cm} (12)
Match the boundary condition \( V(\nu < R) = V(\nu > R) \) at \( \nu = R \):

\[
V(\nu < R) = \frac{2e^2}{4\pi\epsilon_0 \nu^2} \left( \frac{3}{2} - \frac{1}{2} \left( \frac{R}{\nu} \right)^2 \right)
\]

(13)

Now we can compute the perturbative energy shift:

\[
SE_{\nu} = \frac{4\pi\epsilon_0 \rho_{\nu}(0)}{R} \int_{R_0}^{R} \frac{2e^2}{4\pi\epsilon_0 \nu} \left( \frac{3}{2} - \frac{1}{2} \left( \frac{R}{\nu} \right)^2 \right) \nu^2 d\nu
\]

\[
= \frac{2e^2}{\epsilon_0} \frac{\rho_{\nu}(0)}{R} \left( \frac{1}{2} R_0^2 - \frac{1}{2} R^2 \right) = \frac{1}{10\epsilon_0} 2e^2 \rho_{\nu}(0) R^2
\]

\[
SE_{\nu} = \frac{1}{10\epsilon_0} 2e^2 \frac{R^2}{\rho_{\nu}(0)} |\psi_{\nu}(0)|^2
\]

(15)

Add a subscript "\( n \)" to designate that this is the Coulombic energy shift of the \( n^{th} \) nuclear excitation state of the whole nucleus-plus-electrons system.

Given a state, \( \nu \), the so-called isomer shift due to the electron-nucleus interaction depends upon the square of the "size" of the nucleus and upon the electron charge density. \( R_0 \) is not the same for all states, hence the splitting of energy levels in a given species of nucleus depends upon the electron density differences.

Let \( SE_0 \) = isomer effect in ground state

\( SE_1 \) = " " " excited state

\( \Delta E = SE_1 - SE_0 \) = "isomer" shift of energy

\[
= \frac{1}{10\epsilon_0} 2e^2 |\psi_{\nu}(0)|^2 (R_1^2 - R_0^2)
\]

(16)
The "source" material for the Mössbauer gamma ray photons will have some particular electron density at the location of the $^{57}$Fe nuclei: call it $|\Psi_{\text{source}}(0)|^2$ - electron density at source nuclei.

Similarly, the absorber material, due to its differing chemical nature, will have a different density of electrons at its $^{57}$Fe nuclei: Call it $|\Psi_{\text{absorber}}(0)|^2$ - electron density at absorber nuclei.

What we get to measure experimentally is the difference in the isomer shift between source and absorber:

$$\Delta E_{\text{isomer}} = \Delta E_{\text{absorber}} - \Delta E_{\text{source}}$$

$$= \frac{2e^2}{\varepsilon_0} \left( R_1^2 - R_0^2 \right) \left( |\Psi_{\text{absorber}}(0)|^2 - |\Psi_{\text{source}}(0)|^2 \right)$$

What we measure experimentally:

Radii of ground state and excited state.