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Erratum

Core-Electron Contributions to Fe^{57m} Nuclear Quadrupole Interactions in Hemin

Jane C. Chang, T. P. Das and Dennis Ikenberry

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There were a few computational errors in our paper dealing with core-electron contributions to Fe^{57m} nuclear quadrupole interaction in hemin. As a result of these, there are some changes in our calculated core contributions although our general conclusions remain unchanged. We list the appropriate corrected equations and numerical results which should replace the corresponding equations and results stated earlier in the original paper.

In the abstract, the third and fourth sentences should be replaced by: "The distortion of the $3p$ cores by the nitrogen and chlorine atoms are sizeable but their contributions nearly cancel each other in the model chosen for the populations of the atomic orbitals on these atoms. On combining the core contribution with the calculated local contributions reported earlier, the net theoretical result is -0.50 mm/sec." On the last line, we should have 1.20 instead of 1.13 for the contraction ratio, and omit the word "significantly" right after 1.13.

In Eq.(2), a factor of n_j, referring to the number of electrons on the jth orbital, is missing on the right hand side. The corrected form of Eq.(2) is

$$q_{\mathrm{Fe}} = \langle \Psi | q_{\mathrm{Fe}}^{\mathrm{op}} | \Psi \rangle = -\sum_j \langle \psi_j \left| \frac{3\cos^2\theta_{\mathrm{Fe}} - 1}{r_{\mathrm{Fe}}^3} \right| \psi_j \rangle \cdot n_j \tag{2}$$

The statement "n_j is the number of electrons on jth orbital" should be added to the end of the sentence in the second line after Eq.(2).

In Eq.(3), in the numerator on the right hand side, a factor of $\sqrt{n_{iA}/2}$ should be included in the summation term, n_{iA} specifying the number of electrons in the ith orbital of Ath atom. In the denominator of Eq.(3) a factor of $n_{iA}/2$ should be included with the $S^2_{iA,\,3p_z}$ term. Thus Eq.(3) should be read as follows:

$$\psi^{\mathrm{ortho}}_{\mathrm{Fe},\,3p_z} = \frac{\psi_{\mathrm{Fe},\,3p_z} - \sum_{iA} S_{iA,\,3p_z}\chi_{iA}\sqrt{n_{iA}/2}}{\sqrt{1 - \sum_{iA} S^2_{iA,\,3p_z} n_{iA}/2}} \tag{3}$$

The statement "n_{iA} is the number of electrons in the ith orbital of the Ath atom" should be added at the end of the sentence immediately following Eq.(3), that is, after ". . . valence orbitals of atom A". Following the next sentence in the text, ending with ". . . four nitrogen atoms", the following three sentences should be inserted: "For the orbitals of chlorine atom, taking it as a neutral atom with $3s^2 3p^5$ configuration since the effective charge is -0.24 (Jane C. Chang *et al.* "Theory of Isomer Shift in Hemin", Theoret. Chim. Acta (Berl.) (in press)), the value of n_{iA} is 2 for the $3s$ orbitals and 5/3 for each of the $3p_x$, $3p_y$, and $3p_z$ orbitals. For each of the nitrogen atoms with configuration $2s^2 2p^3$, $n_{iA} = 2$ for the $2s$ orbital and 1 for each of the $2p_x$, $2p_y$ and $2p_z$ orbital. For the carbon atom, we shall assume that it has a $2s2p^3$ configuration, applicable for hybridized states, and take $n_{iA} = 1$ for each of the $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals."

The sentence following this, namely "Similar equations . . . $3p_x$, $3p_y$, $2p_x$, $2p_y$ and $2p_z$." should be changed to read: "Similar equations as Eq.(3) hold for the orthogonalized $3p_x$, $3p_y$, $2p_x$, $2p_y$ and $2p_z$ orbitals of iron atom." At the end of the next sentence ". . . on atom A", the statement "and $\psi_{\mathrm{Fe},\,3p_z}$ is the undistorted $3p_z$ orbital of iron atom" should be added.

In Eq.(5), in the first line, on the right-hand side, a factor of 2 should be introduced. Each of the terms in the next three lines should be multiplied by a factor of 2 and also a factor $n_{iA}/2$ should be included inside the summation in the denominator in each of these lines. The revised forms being the following:

$$\begin{aligned} q_{\mathrm{Fe}}^{\mathrm{core}} &= \sum_{i=x,y,z} \langle \psi_{\mathrm{Fe},3p_i}^{\mathrm{ortho}} | q_{\mathrm{Fe}}^{\mathrm{op}} | \psi_{\mathrm{Fe},3p_i}^{\mathrm{ortho}} \rangle \cdot 2 \\ &= \frac{2}{[1-\sum_{iA} S_{iA,3p_z}^2 n_{iA}/2]} \langle 3p_z | q_{\mathrm{Fe}} | 3p_z \rangle \\ &\quad - \frac{1}{[1-\sum S_{iA,3p_x}^2 n_{iA}/2]} \langle 3p_z | q_{\mathrm{Fe}} | 3p_z \rangle \\ &\quad - \frac{1}{[1-\sum_{iA} S_{iA,3p_y}^2 n_{iA}/2]} \langle 3p_z | q_{\mathrm{Fe}} | 3p_z \rangle \end{aligned} \tag{5}$$

Similar changes are made in Eq.(8) as follows:

$$\begin{aligned} q_x^{\mathrm{core}} &= -\frac{\langle 3p_z | q_{\mathrm{Fe}} | 3p_z \rangle}{1-\sum_{ij} S_{iN(j),3p_x}^2 n_{iN(j)}/2 - \sum_{ik} S_{iC(k),3p_x}^2 n_{iC(k)}/2 - \sum_{i} S_{iCl,3p_x}^2 n_{iCl}/2} \\ q_y^{\mathrm{core}} &= -\frac{\langle 3p_z | q_{\mathrm{Fe}} | 3p_z \rangle}{1-\sum_{ij} S_{iN(j),3p_y}^2 n_{iN(j)}/2 - \sum_{ik} S_{iC(k),3p_y}^2 n_{iC(k)}/2 - \sum_{i} S_{iCl,3p_y}^2 n_{iCl}/2} \\ q_z^{\mathrm{core}} &= \frac{2\langle 3p_z | q_{\mathrm{Fe}} | 3p_z \rangle}{1-\sum_{ij} S_{iN(j),3p_z}^2 n_{iN(j)}/2 - \sum_{ik} S_{iC(k),3p_z}^2 n_{iC(k)}/2 - \sum_{i} S_{iCl,3p_z}^2 n_{iCl}/2} \end{aligned} \tag{8}$$

In Eq.(9), for the definition of overlap integrals $S_{iA,3p_j}$ and $S_{iA,2p_j}$, the wave functions χ_{3p_j} and χ_{2p_j} should be changed into ψ_{3p_j} and ψ_{2p_j}.

In Eqs.(10), the first equation should read

$$q_x = q_y = (43.806 + 0.279 + 0.028 + 0.013) a_0^{-3}$$

and the second,

$$q_z = -(87.612 + 0.095 + 0.006 + 0.488) a_0^{-3}$$

Eq.(11) should be changed to the following:

$$\begin{aligned} q_{\mathrm{Fe}}^{\mathrm{core}} &= (0.463 + 0.050 - 0.462) a_0^{-3} \\ &= 0.051 a_0^{-3} \end{aligned} \tag{11}$$

and the three numbers in the line following the equation should be $0.463a_0^{-3}$, $0.050a_0^{-3}$ and $-0.462a_0^{-3}$ instead of the numbers stated before.

In the first line following Table 1 on page 366, $0.28a_0^{-3}$ should be changed to $0.051a_0^{-3}$.

The first three sentences in the last paragraph of page 366 should be replaced by: "The distortion of the $3p$ cores by the nitrogen and chlorine atoms are seen from Eq.(11) to be very sizeable but their contribution nearly cancel each other in the model chosen for the populations of the atomic orbitals on these atoms. The contribution to q due to $2p$ core orbitals is $-1.76 \times 10^{-4} a_0^{-3}$, about 3×10^{-3} of the $3p$ core contribution."

On page 367, the first two sentences should be replaced by: "From the results in the last section it appears that the contribution to the field-gradient from the core orbitals is very significantly influenced by the overlap with neighboring atoms. Since there is a very significant cancellation between the distortion effects due to the influence of the chlorine and nitrogen orbitals, one needs to calculate these effects very carefully. The disagreement between experiment and theory is reduced, but not enough to provide complete agreement."

In the second paragraph on page 367, "the coupling constant $e^2qQ(\mathrm{Fe}^{57\mathrm{m}}) = -0.156$ mm/sec" should be replaced by "the quadrupole splitting $e^2qQ/2(\mathrm{Fe}^{57\mathrm{m}}) = -0.496$ mm/sec" and in the next line, "-0.74 mm/sec" should be followed by a comma and then "the local valence contribution of

-0.573 mm/sec in this paper". Also, the value of χ in the last equation should be quoted as 1.20 instead of 1.13. The last sentence should be replaced by: "However, the important result of the present work is that there can be significant contributions from the core electrons that have to be incorporated in future work in heme and other organic compounds containing iron."

Finally, the following sentence should be added at the end of the paper: "Further, the core contributions should be calculated carefully, in particular making the cores orthogonal to the occupied molecular orbitals rather than using for them the valence orbitals in the atoms as an approximation. We have carried out such a calculation for hemin and obtained a core contribution of 0.148 mm/sec to $e^2qQ/2(Fe^{57m})$. The details of this latter calculation will be published subsequently."

Prof. T. P. Das
Department of Physics
State University of New York at Albany
Albany, New York 12222, USA