1F04　Gauss 軌道を用いて良好な相対論効果の計算が可能か？

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Can the Gaussian-type orbital describe the relativistic calculation well?

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Abstract The relativistic effect is important especially to describe the magnetic resonance spectroscopy. We extend the Kutzelnigg theory and try to solve the relativistic and gauge invariant Dirac equation for the hydrogen atom with using the Foldy-Wouthuysen transformation. On the way for calculating the relativistic quantities, we use the Gaussian-type orbitals in addition to the Slater-type orbital for our aim to apply our theory to molecules and have reached to the title doubt.

Introduction The relativistic usual Dirac equation for the hydrogen atom can be extended to that for including the vector potential of the proton source. The extended Dirac equation is gauge invariant as shown by Sun et al. [1]. However, the gauge invariant Dirac equation has not been solved yet. We try to solve it numerically with using the Foldy-Wouthuysen transformation. We extend the formulation by Kutzelnigg [2] to that for including the vector potential.

Theory The extension of the Kutzelnigg theory can be done as follows: First we extend the momentum $\vec{p}$ to $\vec{\pi} = \vec{p} + e\vec{A}$, so that the gauge invariant Dirac equation is given by $\tilde{H}_D \tilde{\Psi} = \tilde{E}\tilde{\psi}$, where $\tilde{H}_D = mc^2\beta + c\vec{\alpha} \bullet \vec{\pi} + V$ (1), in which the 4 x4 matrices are given by $\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$, and $\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$. The $\vec{\sigma}$ are the 2x2 Pauli spin matrices and 1 is the 2x2 unit matrix. The $c = 137.035999139$ (the speed of light), V is the scalar potential and $\vec{A}$ is the vector potential of the proton source. Applying the Foldy-Wouthuysen transformation given by $\tilde{W}_{FW} = \tilde{W}_a \tilde{W}_b$ to the Dirac Hamiltonian, we have $\tilde{W}_a * \tilde{W}_b * \tilde{H}_D \tilde{W}_a \tilde{W}_b = \begin{pmatrix} \tilde{L}^+ & 0 \\ 0 & \tilde{L}^- \end{pmatrix}$ (2), where $\tilde{W}_a = \begin{pmatrix} 1 & -\tilde{X}^* \\ \tilde{X} & 1 \end{pmatrix}$ and $\tilde{W}_b = \begin{pmatrix} (1+\tilde{X}^*\tilde{X})^{-1/2} & 0 \\ 0 & (1+\tilde{X}\tilde{X}^*)^{-1/2} \end{pmatrix}$. To set the off-diagonal matrix of the Dirac equation be zero, the matrix $\tilde{X}$ must be satisfied the following equation:

$$2mc^2\tilde{X} = c\vec{\sigma}\bullet\vec{\pi} + V\tilde{X} - \tilde{X}V - \tilde{X}c\vec{\sigma}\bullet\vec{\pi}\tilde{X} \quad (3).$$

Instead of solving Eq. (3), we use a perturbation expansion given by

$$\tilde{X} = c^{-1}(\tilde{X}_0 + c^{-2}\tilde{X}_2 + c^{-4}\tilde{X}_4 + \bullet\bullet\bullet) \text{ where } \tilde{X}_0 = (1/2m)\vec{\sigma}\bullet\vec{\pi} \quad (4).$$

The other quantities can be given by

$$\tilde{L}^+ = mc^2 + \tilde{L}_0^+ + c^{-2}\tilde{L}_2^+ + c^{-4}\tilde{L}_4^+ + \bullet\bullet\bullet \text{ where } \tilde{L}_0^+ = \tilde{H}_0 \quad (5), \text{ and}$$

$$\tilde{E} = mc^2 + \tilde{E}_0 + c^{-2}\tilde{E}_2 + c^{-4}\tilde{E}_4 + \bullet\bullet\bullet \text{ where } \tilde{E}_0 = <\phi_0 | \tilde{L}_0^+ | \phi_0> = <\phi_0 | \tilde{H}_0 | \phi_0> \quad (6).$$

Results To calculate quantities defined by Eq. (6), we use the finite nucleus model to avoid the divergent integrals arising in them.

Table 1 Results for the hydrogen atom with using the STO-NG expansion of the 1s-Slater-type orbital, ϕ_0, and with using the finite nucleus models

The value of $(1/4m^2c^2) <\phi_0 | i\vec{\sigma}\bullet(\vec{p}V\times\vec{A} + \vec{A}V\times\vec{p}) | \phi_0>$

	For SSCDD model		For HCDD model		For GCDD model	
N	Value	Rel. error	Value	Rel. error	Value	Rel. error
12	0.1990(-2)	0.203(-1)	-0.1471(-6)	0.854	-0.1469(-6)	0.855
18	0.2022(-2)	0.485(-2)	-0.2040(-6)	0.797	-0.2032(-6)	0.799
24	0.2029(-2)	0.134(-2)	-0.2532(-6)	0.748	-0.2507(-6)	0.752
30	0.2031(-2)	0.365(-3)	-0.2978(-6)	0.704	-0.2906(-6)	0.713
∞	0.2032(-2)		-0.1005(-5)		-0.1012(-5)	

The value with using the 1s-Slater orbital is denoted by $N = \infty$.

The STO-30G gives only half significant figures for the GCDD model, in spite of that it gives 15 significant figures for the two-center Coulomb integral. This is the example of the worst precision among all of $<\phi_0 | (1/c^2)\tilde{L}_2^+ | \phi_0>$ and $<\phi_0 | (1/c^4)\tilde{L}_4^+ | \phi_0>$.

The other results and the discussion will be shown in the slide.

Conclusion We conclude that the Gaussian-type orbital can not describe the relativistic calculation well, especially for quantities such as the divergent integrals which are arising in our theory for calculating the magnetic resonance spectroscopy.

[1] W-M Sun, X-S Chen, X-F Lü, and F. Wang, Phys. Rev. A82, 012107 (2010)

[2] W. Kutzelnigg in “Relativistic electronic structure theory” Part 1, edited by P. Schwerdtfeger, (Elsevier Amsterdam 2002) pp.664.

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