Electronic Structure Calculation of Muonium in Silicon

KANAZAWA UNIVERSITY

Abstract

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シリコン中ミュオニウムの電子構造計算

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Doctor of Philosophy in Science

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by Muhamad Nasruddin Manaf

We present calculation of electronic structure of muonium in silicon in particular anomalous muonium which has been extensively studied but there is still unresolved problems in first-principles calculations. We perform calculations by using spin-polarized density functional theory within the general gradient approximation or the local density approximation. We check the size effect of supercells and find that we need to use large sizes of supercells to get reliable results. Some quantitative disagreement between the experimental and theoretical values in previous studies may be due to the use of insufficient sizes of supercells. We clarify that the negative Fermi contact interaction constant (FCIC) is induced by the electron correlation effect; By using the Hubbard model, we find that the FCIC is zero when we neglect the correlation effect and the negative value of the FCIC is induced by the correlation effect.

Keywords: silicon, muonium, supercells and correlation effect

Purposes of This Study

The muonium in silicon is the benchmark for study of muonium in semiconductor [1-13]. It has been recognized that the muonium in silicon can be located at bond-center or at the tetrahedral site. The muonium located at the bond-center site is commonly recognized as an anomalous muonium. The anomalous muonium has been already observed by experiment [4]. Unfortunately, theoretical studies have not explained yet, in particular for anomalous muonium. Therefore in this study we provide reliable calculation by using density functional theory (DFT) and successfully explain the origin of the small and negative value of muonium which is considered as an unresolved problem.

We focus our study about firs-principles study of muonium in silicon using DFT in particular muonium at bond center (BC). In this thesis we focus on the study of the hyperfine parameters, in particular FCIC. We try to determine the calculation parameters and vary the size of supercells, where we try to increase the accuracy of the calculation results because there is discrepancy between result of experiment and theoretical calculation in the past [8,9,12]. We also explain the origin of small and negative value of FCIC in the case of anomalous muonium in silicon, which is considered as an unresolved problem. We consider to use the Hubbard model by using three linear hydrogen to explain that the origin of the small and negative values in anomalous muonium, of the electron correlation.

Calculation Method

First-principles calculations based on the spin-polarized density-functional theory are carried out by using PHASE/0 code [14-17]. In this calculation, we use a supercell approximation to study muonium in silicon crystals [1,18]. The norm-conserving pseudopotential developed by Troullier and Martins is used for both atoms [19]. We set the cut off energies of 25 Rydberg and 100 Rydberg, respectively, for the wavefunctions and charge density. We use the local density approximation (LDA) and the generalized gradient approximation (GGA) for the exchange-correlation energy. The LDA calculation is based on the method developed by Perdew and Wang [20] and we use the Perdew-Burke-Ernzerhof formalism for the GGA calculations [21].

The lattice parameter of the unit cell is set to be 5.431 Å which is deduced from experimental data [22-24]. We vary the size of the supercell, and then we check the convergence of the FCIC. We adopt the Γ k point sampling for supercell calculations. We optimize the atomic geometries and in the optimized geometry, the atomic forces are less than 10^{-3} Hartree/Bohr and the total energy is converged within 10^{-10} Hartree/cell. By using the k points of the 4×4×4 mesh grid, we apply the tetrahedron method to the calculations of density of states (DOS) and projected density of states (PDOS).

Results and Discussion

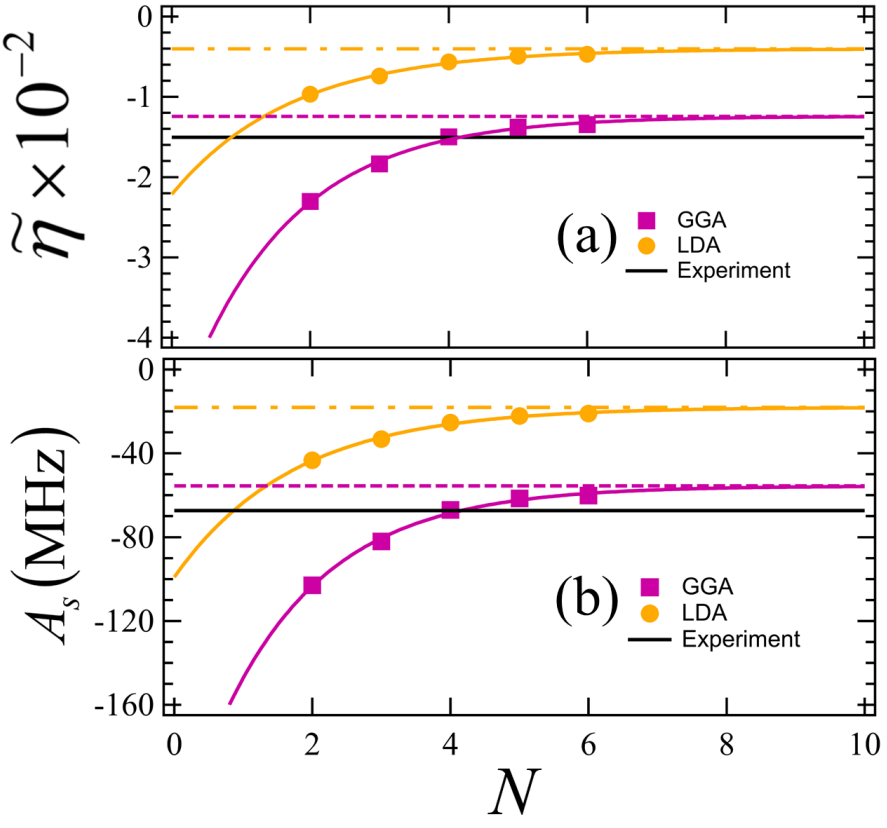

Figure 1: (a) Calculated $\tilde{\eta}$. The black solid line represents η deduced from experimental data[3]. We present the fitting curves for the LDA and GGA calculational results. (b) Calculated FCIC. The experimental value is deduced from Ref. 3 and is represented by the black solid line. The horizontal axis represents N which means that the supercell size is $N \times N \times N$.

We first determine the stable position of muonium and confirm that the BC site is the most stable. We next calculate the FCIC (Fig. 1(a) and (b)). The constant

reaches the convergence by using the supercell of the 4×4×4 size: the supercell gives the value close to these calculated by using from the 5×5×5 and 6×6×6 supercells. We find that the following function well fits to the above mentioned FCIC and $\tilde{\eta}$:

$$Y_{FCIC} = A + B\exp(-\alpha N), \tag{1}$$

$$Y_{\tilde{\eta}} = A' + B'\exp(-\alpha' N). \tag{2}$$

where N is the supercell parameter, which means that the supercell size is $N \times N \times N$. All fitting parameters can be seen in Table 1.

Table 1: Fitting parameters in Eq. (1) and Eq. (2)

Exchange Energy	A(MHz)	B(MHz)	α	A'	B'	α'
GGA	-55.6	-175.6	0.65	-0.012	-0.039	0.651
LDA	-18.0	-81.1	0.57	-0.004	-0.018	0.577

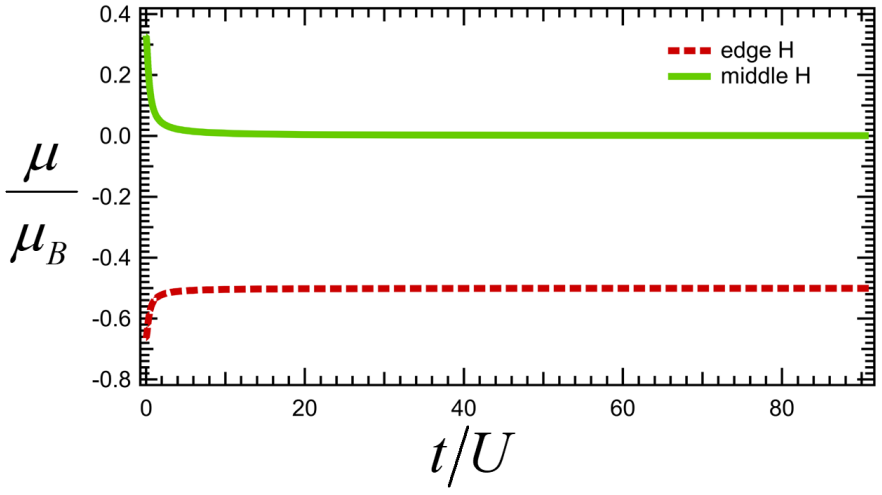

Figure 2: The magnetic moment of electrons based on the Hubbard model of three linear hydrogen molecule.

Our calculation shows that the FCIC is negative, which is due to the fact that the spin density at the muon site is negative. We here discuss the origin of this negative spin density at the muon site. We introduce the Hubbard model for linear tri-hydrogen molecule, which is considered to be a simplified model of the present system [25]. We numerically solve the Hubbard model in the case of $\frac{t}{U} \to 0$, and find that the magnetic moments at the middle site and the side sites have the opposite signs; The magnetic moment at the middle site and the edge sites are $\frac{1}{3}\mu_B$ and -$\frac{2}{3}\mu_B$, respectively (see Fig. 2 and Fig. 3), which means that the spin density at the middle site is negative. We perform GGA calculation by taking

a large bond length(l_{H-H} = 2.0 Å), which corresponds to a small $\frac{t}{U}$ case in the Hubbard model (see Fig. 3). The calculated spin density distribution is similar to that in the Hubbard model in the limit, $\frac{t}{U} \to 0$. As $\frac{t}{U}$ becomes large, the magnitude of the spin density at the middle site is expected to decrease and get close to zero as is expected based on the tight binding model. This tendency of the spin density expected based on the Hubbard model is reproduced by our GGA calculation. We perform calculations for the bond lengths of 0.82 Å, 0.95 Å and 2.00 Å and find that the magnitude of the spin density at the middle site becomes small as the bond length decreases(Fig. 3). Finally, by considering the analogy between the linear tri-hydrogen molecule and the present system, we attribute the negative FCIC to the electron correlation effect.

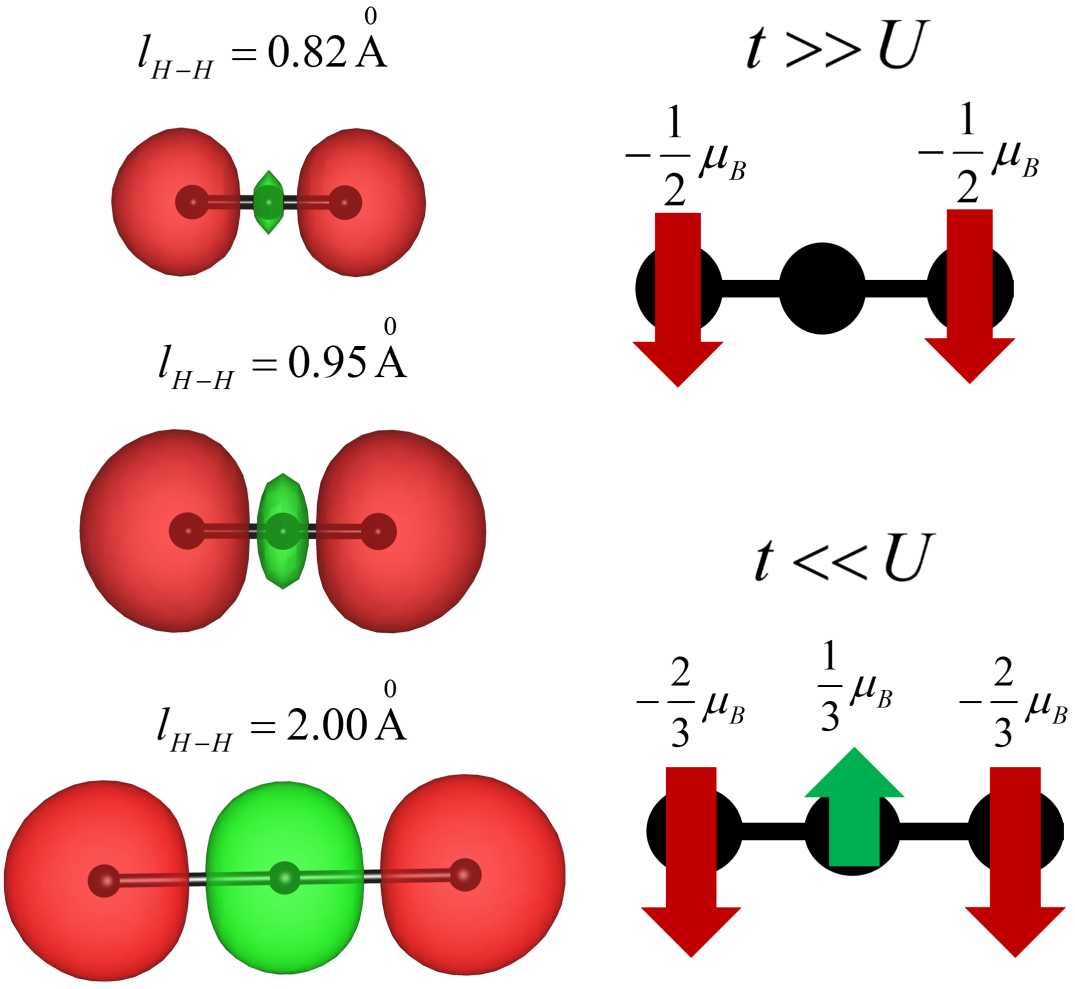

Figure 3: Spin densities of the linear tri-hydrogen molecule (the red and the green colors represent positive and negative value of isosurfaces, respectively) for the cases of l_{H-H}= 0.82 Å (the isosurface value is 9.11×10^{-2} spin/bohr^{-3}), l_{H-H}=0.95 Å (the isosurface value is 4.11×10^{-2} spin/bohr^{-3}), and l_{H-H}=2.0 Å (the isosurfacevalue is 4.11×10^{-2} spin/bohr^{-3})(The spin density was drawn using VESTA [26,27]). We also show the magnetic moment at each site calculated based on the Hubbard model. Two limiting cases ($t >> U$ and $t << U$) are considered.

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令和　元年　7月　31日

学位論文審査報告書（甲）

1．学位論文題目（外国語の場合は和訳を付けること。）

Electronic Structure Calculation of Muonium in Silicon

シリコン中ミュオニウムの電子構造計算

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3．審査結果の要旨（600～650字）

半導体中で水素不純物は、ドーパントの不活性化や浅い不純物準位生成によるキャリアの供給等、多様な影響を与えるためその制御が重要である。陽子と同じ電荷を持つミュオンと電子からなるミュオニウムは物質中で水素と同様の振る舞いをすると予想される事から、ミュオンスピン回転法は、物質中の水素を研究する上で重要な手段となっている。この実験手法の結果から正確な情報を引き出すために、第一原理に基づく信頼性の高いシミュレーションの実行が必要である。この点を考慮し本研究では、これまでに多くの研究がなされてきたシリコン中ボンド中心に位置するミュオニウムを取り上げ、フェルミ接触項の密度汎関数理論に基づく計算を行った。大規模スーパーセル計算を行い、収束した結果を得るには、大きなセルサイズの計算が必要である事を明らかにし、過去における計算値と実験値の食い違いがセルサイズの問題によって生じていることを示唆した。本計算は、負の値を持つフェルミ接触項の実験値を良く再現し、密度汎関数理論に基づく計算手法の信頼性を確立した。また、線形3原子水素分子に対するモデル計算から中央の水素原子に負のスピン密度が生じるのは電子相関によるものであることをつきとめた。この線形分子とボンド中心にミュオンが位置する本系との類似性から、ミュオニウムサイトのスピン密度が電子相関により負となる事を明らかにし、負のフェルミ接触項の原因となる事を結論した。本研究は、今後のミュオン科学分野の研究に有用な知見を与えるものであると判断し、博士論文の研究としてとして適切であると結論する。

4．審査結果　(1) 判　　定（いずれかに○印）　（合　格）・　不合格

(2) 授与学位　　博　士（　理学　）