PHYSICAL REVIEW B VOLUME 39, NUMBER 8 15 MARCH 1989-I

Localized-orbital approach to the electronic structure of anomalous muonium in diamond

Toshiharu Hoshino and Toshio Asada
Department of General Education, College of Engineering, Shizuoka University, Hamamatsu 432, Japan

Kiyoyuki Terakura
Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

(Received 20 September 1988)

Characteristics of the electronic structure of anomalous muonium in diamond are investigated based on the relaxed-bond-centered (RBC) model by use of a self-consistent Green's-function method within the local-spin-density-functional formalism. A minimal basis set of well-contracted localized orbitals determined from first principles is used. For the case of 42% stretched C—C bond length, calculated values of -137 and 400 MHz for the Fermi-contact and dipolar hyperfine parameters, respectively, give good agreement with the experimental values of -206 and 374 MHz, strongly supporting the RBC model. A simple interpretation is also given of the mechanism for the negative Fermi-contact hyperfine parameter.

The muon-spin-rotation (μSR) experiments have revealed that in five semiconductors, diamond,[1] Si,[2,3] Ge,[4] GaP,[5] and GaAs,[5] the positive muon (μ^+) forms two distinct types of muonium (μ^+e^-) centers, designated as normal and anomalous muonium, Mu and Mu*. Mu is characterized by a large isotropic hyperfine (hf) parameter about half the free-muonium value,[1-5] whereas Mu* has far smaller and highly anisotropic parameters with $\langle 111 \rangle$ axial symmetry. Mu is considered to be moving rapidly in a crystal,[6-8] but Mu* is not. Mu* in diamond is believed to be definitely more stable than Mu.[1,9,10] Recent theoretical studies[11-13] suggest that Mu hops mostly among tetrahedral interstitial sites. However, there has been considerable debate on the location of Mu*. Among several models proposed so far,[14-19] two have received considerable theoretical studies. In one, Mu* is assumed to be trapped near a double positively charged vacancy [vacancy-associated (VA) model],[18,19] and in the other, it is considered to be a neutral interstitial occupying a bond center with an unusually large lattice relaxation[13,17,20] [relaxed-bond-centered (RBC) model]. On the VA model, Sahoo *et al.*[19] obtained for diamond, by an unrestricted Hartee-Fock (HF) cluster calculation, -85 and 139 MHz for the Fermi-contact hf parameter (isotropic, called A) and the dipolar one (anisotropic, called $2B$), respectively, whereas on the RBC model for an optimized C—C separation stretched by 42%, Estle *et al.*,[20] obtained ~ -850 MHz for A using a cluster HF method with an approximation known as partial retention of diatomic differential overlap. The experimental values of A and $2B$ are -206 and 374 MHz, respectively. The calculated values of A differ very much from each other and both apparently deviate a great deal from the experimental value. However, the HF method generally overestimates spin polarization. Thus the calculated values of A might considerably decrease when correlation effects are taken into account.[11,20,21] Therefore, the situation on A's seems to be more favorable to the RBC model. Though the value of A might be somehow delicate since it reflects the spin density only at one point, i.e., the μ^+ site, the dipolar parameter $2B$ would be more stable because it reflects $\langle r^{-3} \rangle$, the mean inverse cube of the separation between μ^+ and an unpaired electron. Though Estle *et al.*[20] did not give $2B$, their equilibrium C—Mu*—C separation will hopefully give a value for $2B$ in reasonable agreement with the experimental value.[17] On the other hand, the value 139 MHz obtained using the VA model is too small, which is estimated to correspond to a mean separation roughly the same as the bulk bond length, as is expected from the atomic configuration of the VA model. Therefore the experimental results seem to be much more favorable to the RBC model. Moreover, recent success by Kiefl *et al.* in level-crossing-resonance (LCR) spectroscopy on Mu* in Si (Ref. 22) and GaAs (Ref. 23) seems to decisively substantiate the above conjecture. By resolving ^{29}Si hf structure they found that for Mu* in Si (GaAs) most of the electron-spin density is on the nearest-neighbor two equivalent Si atoms (Ga and As) on the $\langle 111 \rangle$ symmetry axis. Taking the above theoretical studies into account, these LCR results seem to establish that Mu* is located at the bond center in all five semiconductors discovered so far.

The purpose of the present paper is to investigate the electronic structure of the RBC model of Mu* in diamond with the degree of stretching varied around 42%, by a more sophisticated tool than the cluster HF method used so far and to examine a detailed comparison with the experimental results. We approach the problem with a self-consistent-field Green's-function method[24-26] within the local-spin-density-functional formalism. We use for the exchange-correlation potential Ceperley and Alder's interacting electron-gas results[27] as interpolated by Perdew and Zunger.[28] The carbon atom is treated by the norm-conserving pseudopotential[29] (NCP), but the muonium is treated by the all-electron potential. The matrix approach with an adspace technique[30] is adopted. Accuracy of the present calculation is governed by both the quality of the basis set and the range of the impurity region included in solving Dyson's equation. In practice, the range of the impurity region does depend on the degree of extension of local orbitals taken as basis functions. We therefore employ a minimal basis set composed of well-contracted localized orbitals (LO's) for both perfect and defect crystals, prepared according to the prescription developed by the present authors.[31,32] It contributes considerably to saving computational time with little cost in accuracy. Though this paper is the first application of the LO's to crystalline materials, details will be discussed in a planned later publication. LO's are represented by Gaussian-type orbitals, and Refs. 24–26 and 33 were consulted for some details of the calculational procedure. The impurity region C_8Mu^* employed in this calculation is illustrated in Fig. 1, where the potential is determined self-consistently. Two equivalent carbon atoms, labeled C(1), are relaxed outward along the $\langle 111 \rangle$ axis with other six C(2) atoms fixed at the bulk location. Three kinds of LO's, one (1*s*-type) LO at a Mu* site and two (2*s*- and $2p_x$-type) LO's at each C(1) site, are determined for every given relaxation, with the bulk LO's fixed at C(2) sites, where the *x* axis is taken in the [100] direction. The appearance of only one kind of 2*p*-type LO results from having neglected possible mixing between 2*s*- and 2*p*-type LO's in the present treatment.

In Figs. 2(a) and 2(b) we illustrate radial profiles of the 2*s*- and $2p_x$-like LO's, respectively, used in calculating bulk Green's functions, and in Fig. 2(c) the 1*s*-like LO at Mu* for the 42% stretched C(1)—C(1) separation. The corresponding atomic orbitals (AO's) are shown for comparison. As the LO's for the C(1) site differ only slightly from the bulk LO's, they are not shown here. We observe large contractions in the LO's from the corresponding AO's. In Fig. 3(a) we show density of states (DOS) of diamond, calculated self-consistently by use of the above LO basis set. The valence-band width and the band gap are 21.46 and 5.80 eV, respectively. The valence-band width agrees very well with 21.45 eV obtained by a NCP plane-wave calculation,[34] whereas our band gap is roughly 50% larger than the plane-wave result. In Figs. 3(b) and 3(c) we show the changes in DOS for each spin, caused by the muonium at the center of C(1)—C(1) bond stretched by 42%. There appears one gap state for each spin around the middle of the band gap with only the one for up spin occupied, and a broad decrease and increase in higher- and lower-energy parts, respectively, of the valence-band region. We observe a sharp nearly localized state for each spin at the conduction-band bottom.

Figure 4(a) shows charge densities along the $\langle 111 \rangle$ axis: $n_{\text{gap}}(r)$ coming from the gap state and $n_{\text{val}}(r)$ from the total perturbed energy distribution in the valence-band-energy region. The gap state is composed almost exclusively of C(1) *p* orbitals and has an antibonding character, resulting in vanishing amplitude at the muon site. The characteristic abundance of the *p* component in the gap state is a consequence of the large outward displacement of C(1) sites, which resembles what occurs on

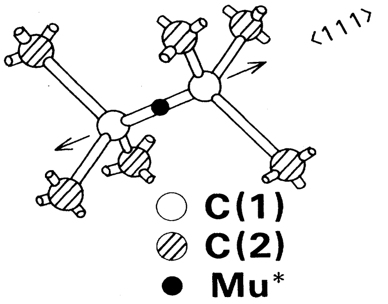

FIG. 1. Atomic configuration in the C_8Mu^* cluster employed as an impurity region. Arrows indicate the directions of displacement of C(1) atoms.

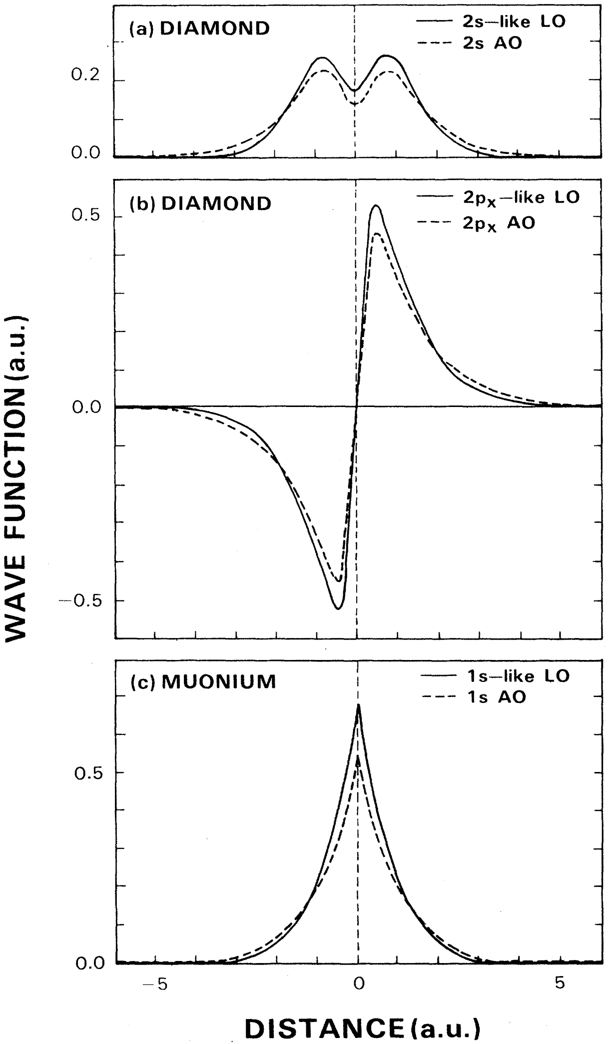

FIG. 2. (a) The 2*s*-like LO of a carbon atom in diamond, together with the 2*s* AO shown by a dashed line. (b) The $2p_x$-like LO of a carbon atom in diamond, together with the $2p_x$ AO shown by a dashed line. (c) The 1*s*-like LO of Mu* for the atomic configuration of C(1)—C(1) separation stretched by 42%. The 1*s* AO is shown by a dashed line.

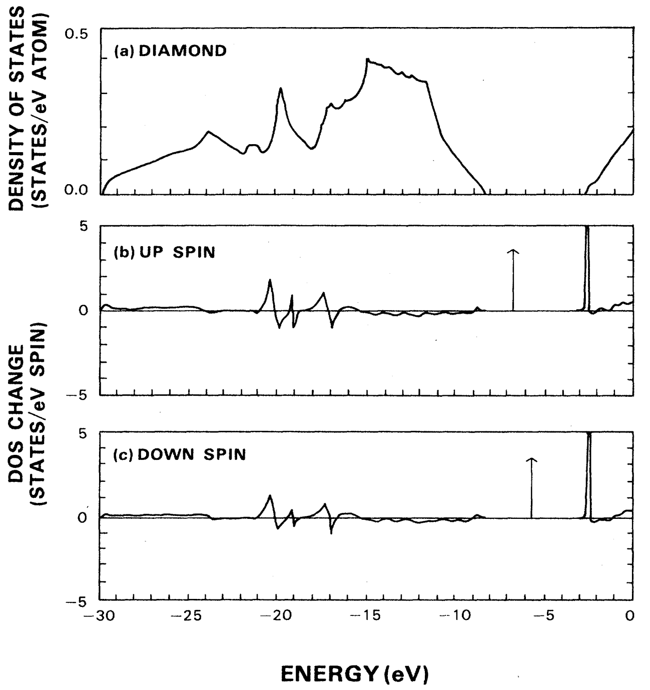

FIG. 3. (a) DOS of diamond calculated self-consistently by use of a minimal basis set of LO's shown in Figs. 2(a) and 2(b). (b) Change in DOS for spin up. The gap state is occupied. (c) Change in DOS for spin down. The gap state is empty.

dangling bonds of semiconductor surface atoms.[35] By Mulliken charge analysis of the gap state, we find that 83% of the charge is localized on the two C(1) sites and that the impurity region C_8Mu^* contains 91% of the charge. The gap state is localized almost completely within the present impurity region. We therefore believe that the cluster of Fig. 1 is large enough to deal with the hf parameters, since the quantities are governed essentially by this gap state. The profile of $n_{\text{val}}(r)$ suggests that there is a strong three-centered bonding state C(1)—Mu*—C(1) constructed with a certain amount of energy gain expected from the valence-band DOS redistribution shown in Figs. 3(b) and 3(c). We find that the very sharp peak at the conduction-band bottom for each spin corresponds to an antibonding state which has principal amplitudes on Mu* and two C(1) sites. These situations substantiate the chemical and intuitive consideration by Cox and Symons.[17]

Regarding hf parameters, we first note that the spin polarization of the gap state does not make any direct contribution to A as suggested first by Symons.[16] Only the polarization of valence-band wave functions can contribute to A and thereby the absolute value of A is very small. To see the mechanism of negative polarization ($A<0$), we plot the exchange-correlation potentials $V_{\text{xc}}^{\uparrow}(r)$ and $V_{\text{xc}}^{\downarrow}(r)$ in Fig. 4(b). The significant difference between them at the C(1) sites comes from the gap-state polarization. Responding to larger but negative $V_{\text{xc}}^{\uparrow}(r)$, spin-up electrons, which had originally identical density with that of spin down, redistribute to gain the potential decrease more than spin-down electrons. This wave-function polarization, which results in negative spin polarization at μ^+, outweighs a positive contribution coming from the small spin polarization of the valence band within the impurity region.[36] On the other hand, the major contribution to the dipolar term $2B$ comes from the gap-state polarization.[36]

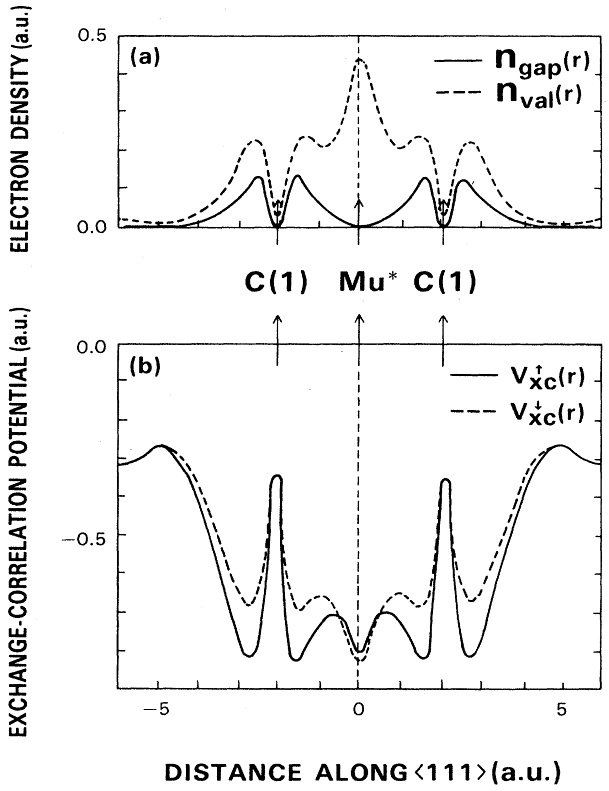

FIG. 4. (a) Charge densities along the ⟨111⟩ axis, $n_{\text{gap}}(r)$ and $n_{\text{val}}(r)$, from the gap state and the valence-band states, respectively. (b) Exchange-correlation potentials $V_{\text{xc}}^{\uparrow}(r)$ and $V_{\text{xc}}^{\downarrow}(r)$ along the ⟨111⟩ axis.

In Table I we give calculated values of A and $2B$ for C(1)—C(1) separation varied around 42%, together with the experimental values. We see that A does not depend much on the separation, but that $2B$ does, as it should. In order to compare the calculated values with the experimental ones, we have to consider the effect of vibrational motion of Mu* on the hf parameters. Claxton *et al.*[37]

TABLE I. Calculated values of A and $2B$ for three different C(1)—C(1) separations, together with the experimental ones. λ indicates the degree of stretching of the C(1)—C(1) separation.

	λ (%)			
	40	42	44	Expt.[a]
A (MHz)	−136.4	−137.0	−137.4	−206
$2B$ (MHz)	429.1	400.1	372.9	374

[a] Reference 1.

calculated a change in A by use of the cluster HF method, with the muonium site displaced perpendicularly away from the bond center for a fixed C(1)—C(1) separation stretched by 44%, in the direction along which the principal vibrational motion will occur. They showed that the change is almost negligible. Therefore, the effect of the vibrational motion on A may be quite small. On the other hand, its effect on $2B$ will make the value smaller since the distance between μ^+ and an unpaired electron becomes larger for the movement of muonium in these directions. We therefore expect that the vibrational average of the calculated values for a 42% stretched C(1)—C(1) separation would lead to a better agreement with the experimental values. We think that an excellent reproduction of $2B$ gives strong support to the RBC model employed here.

In this work we could not give a determination of the equilibrium relaxation by total-energy minimization, since our impurity region, even for the limited relaxation mode given here, is not large enough for the total-energy argument. We have to include all atoms at least up to second nearest to the displaced atoms to achieve the total-energy minimization, taking correctly into account the energy increase due to the bond bending on the outer atoms [C(2) in Fig. 1]. The calculation on a larger cluster $C_{26}Mu^*$, which suffices for this requirement, is under study. LCR spectroscopy on diamond is expected to give a direct experimental test on the gap state obtained in this calculation.

Numerical computations were carried out with the computers at the Institute for Molecular Science. The work was supported in part by the Ministry of Education, Science and Culture, Japan (No. 63540245).

---

[1] E. Holzschuh, W. Kündig, P. F. Meier, B. D. Patterson, J. P. F. Sellschop, M. C. Stemmet, and H. Appel, Phys. Rev. A **25**, 1272 (1982).

[2] J. H. Brewer, K. M. Crowe, F. N. Gygax, R. F. Johnson, B. D. Patterson, D. G. Fleming, and A. Schenck, Phys. Rev. Lett. **31**, 143 (1973).

[3] B. D. Patterson, A. Hintermann, W. Kündig, P. F. Meier, F. Waldner, H. Graf, E. Recknagel, A. Weidinger, and Th. Wichert, Phys. Rev. Lett. **40**, 1347 (1978).

[4] E. Holzschuh, H. Graf, E. Recknagel, A. Weidinger, Th. Wichert, and P. F. Meier, Phys. Rev. B **20**, 4391 (1979).

[5] R. F. Kiefl, J. W. Schneider, H. Keller, W. Kündig, W. Odermatt, B. D. Patterson, K. W. Blazey, T. L. Estle, and S. L. Rudaz, Phys. Rev. B **32**, 530 (1985).

[6] B. D. Patterson, E. Holzschuh, R. F. Kiefl, K. W. Blazey, and T. L. Estle, Hyperfine Interact. **17-19**, 599 (1984).

[7] K. P. Döring, K. P. Arnold, M. Gladisch, N. Haas, E. E. Haller, D. Herlach, W. Jacobs, M. Krause, M. Krauth, H. Orth, and A. Seeger, Hyperfine Interact. **17-19**, 629 (1984).

[8] C. W. Clawson, K. M. Crowe, E. E. Haller, S. S. Rosenblum, and J. H. Brewer, Hyperfine Interact. **17-19**, 603 (1984).

[9] B. D. Patterson, E. Holzschuh, W. Kündig, P. F. Meier, W. Odermatt, J. P. F. Sellschop, and M. C. Stemmet, Hyperfine Interact. **17-19**, 605 (1984).

[10] W. Odermatt, Hp. Baumeler, H. Keller, W. Kündig, B. D. Patterson, J. W. Schneider, J. P. F. Sellschop, M. C. Stemmet, S. Connell, and D. P. Spencer, Hyperfine Interact. **32**, 583 (1986).

[11] S. Estreicher, A. K. Ray, J. L. Fry, and D. S. Marynick, Phys. Rev. B **34**, 6071 (1986).

[12] N. Sahoo, S. K. Mishra, K. C. Mishra, A. Coker, T. P. Das, C. K. Mitra, L. C. Snyder, and A. Glodeanu, Phys. Rev. Lett. **50**, 913 (1983).

[13] S. Estreicher, Phys. Rev. B **36**, 9122 (1987).

[14] T. L. Estle, Hyperfine Interact. **8**, 365 (1981).

[15] B. D. Patterson, Hyperfine Interact. **18**, 517 (1984).

[16] M. C. R. Symons, Hyperfine Interact. **17-19**, 771 (1984).

[17] S. F. J. Cox and M. C. R. Symons, Chem. Phys. Lett. **126**, 516 (1986).

[18] T. L. Estle, Hyperfine Interact. **17-19**, 585 (1984).

[19] N. Sahoo, K. C. Mishra, and T. P. Das, Phys. Rev. Lett. **55**, 1506 (1985).

[20] T. L. Estle, S. Estreicher, and D. S. Marynick, Phys. Rev. Lett. **58**, 1547 (1987).

[21] S. Estreicher, A. K. Ray, J. L. Fry, and D. S. Marynick, Phys. Rev. Lett. **57**, 3301 (1986).

[22] R. F. Kiefl, M. Celio, T. L. Estle, S. R. Kreitzman, G. M. Luke, T. M. Riseman, and E. J. Ansaldo, Phys. Rev. Lett. **60**, 224 (1988).

[23] R. F. Kiefl, M. Celio, T. L. Estle, G. M. Luke, S. R. Kreitzman, J. H. Brewer, D. R. Noakes, E. J. Ansaldo, and K. Nishiyama, Phys. Rev. Lett. **58**, 1780 (1987).

[24] G. A. Baraff and M. Schlüter, Phys. Rev. B **19**, 4965 (1979).

[25] J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. B **21**, 3545 (1980).

[26] G. A. Baraff and M. Schlüter, Phys. Rev. B **30**, 1853 (1984).

[27] D. M. Ceperly and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[28] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[29] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[30] A. R. Williams, P. J. Feibelman, and N. D. Lang, Phys. Rev. B **26**, 5433 (1982).

[31] T. Hoshino, T. Asada, and K. Terakura, Phys. Rev. B **31**, 2005 (1985).

[32] T. Hoshino, T. Asada, and K. Terakura, Phys. Rev. B **34**, 8933 (1986).

[33] P. J. Feibelman, J. Chem. Phys. **81**, 5864 (1984).

[34] G. B. Bachelet, H. S. Greenside, G. A. Baraff, and M. Schlüter, Phys. Rev. B **24**, 4745 (1981).

[35] W. A. Harrison, Surf. Sci. **55**, 1 (1976).

[36] Calculated value of an excess number of spin-up electrons coming from the valence-band region is 0.05 within the impurity region, whereas 0.91 is from the gap state.

[37] T. A. Claxton, A. Evans, and M. C. R. Symons, J. Chem. Soc., Faraday Trans. 2 **82**, 2031 (1986).