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# Calculation of positron states in carbon-nanotube bundles

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**Abstract**

Positron distributions and lifetimes in carbon-nanotube bundles have been calculated using a combination of the superposed-neutral-atom model and the finite-difference method (SNA-FD) as well as with an *ab initio* method. The electron–positron correlation was described with the local density approximation (LDA) or the generalized gradient approximation (GGA). For the LDA, the SNA-FD and *ab initio* calculations give similar results. Positrons are predominantly distributed in interstitial regions for smaller-size nanotubes, while they are distributed inside nanotubes for larger sizes. The estimated positron lifetime ranges from 250 to 480 ps as a function of the nanotube diameter. In contrast to this, for the GGA, the SNA-FD and *ab initio* calculations give quite different results concerning the positron distribution and lifetime.

## 1. Introduction

Single-wall carbon nanotubes (SWNTs) [1], which have the form of a rolled graphite sheet, show various electronic properties from metallic to semiconducting depending on the diameter and chirality [2]. Recently, bundles of SWNTs were synthesized by the laser ablation technique. It was found that SWNTs are arranged to form a trigonal lattice in the plane perpendicular to the tube axis [3]. In the SWNT bundle, there are two kinds of large open space; one is the interstitial region and the other is the inside of the SWNT. The situation is similar to that for solid $C_{60}$. It is thought that the electronic structure of the SWNT bundle can be modified by doping atoms or molecules into these open spaces.

Positrons are known to be selectively distributed in open spaces in solids. It is an interesting problem to find in which open space positrons are distributed, the interstitial site or the inside. So far, a few positron lifetime studies have been made for multi-wall carbon nanotubes (MWNTs). Ito and Suzuki [4] reported a single-component positron lifetime of 387 ps. Details about the MWNT samples were not given. Fukutomi *et al* [5] reported a lifetime value of 382 ps for MWNTs with diameters of a few hundred ångströms. They ascribed the observed lifetime to annihilation at the MWNT surface. Ohdaira *et al* [6] reported a somewhat shorter value of 355 ps. They made measurements on an oriented MWNT film prepared by the chemical

  

vapour deposition (CVD) technique on a Si substrate. The typical diameter of MWNTs was reported as 400 Å. Each MWNT consists of more than 40 nanotubes.

## 2. Calculations

### *2.1. The superposed-neutral-atom model and the finite-difference method*

A set of calculations have been performed with the superposed-neutral-atom model and the finite-difference method (SNA-FD) developed by Puska and Nieminen [7]. The electronic charge density and the electrostatic potential are described as the superposition of neutral-atom electron densities and potentials.

For the electron–positron correlation energy, we used the interpolation formulae given by Boroński and Nieminen [8] in the local density approximation (LDA) framework as well as the generalized gradient approximation (GGA) formula proposed by Barbiellini *et al* [9, 10].

The positron Schrödinger equation can be solved by the numerical relaxation technique proposed by Kimball and Shortley [11]. The differential equation is replaced by a set of linear algebraic equations on a set of three-dimensional mesh points.

Positron lifetimes were calculated with the Brandt–Rheinheimer [12] enhancement factor for valence electrons (2s2p) and with a constant value of 1.5 for core electrons (1s) for the LDA. For the GGA, the expression given by Barbiellini *et al* [9, 10] was used.

The calculations were made on bundles of seven kinds of *zigzag* SWNT with indices of $(n, 0)$ ($n = 6$–12) as well as seven kinds of *armchair* SWNT with indices of $(n, n)$ ($n = 4$–10). We follow the definition of the index $(n, m)$ described in [13]. We used the computational codes in [13] to generate the positions of carbon atoms. The C–C bond length was taken as 1.42 Å. The inter-tube distance (surface to surface) was assumed to be 3.30 Å, referring to the theoretical results by Okada *et al* [14]. They predicted values of 3.17, 3.30 and 3.32 Å for the (6, 0), (6, 6) and (12, 0) bundles, respectively. Experimentally, a slightly smaller value of 3.15 Å was suggested for the (10, 10) bundle [3]. For comparison, we made calculations also on several kinds of bundle with the inter-tube distance of 3.15 Å.

### *2.2. The ab initio method*

The other set of calculations were performed with an *ab initio* method. The valence electronic charge density was obtained as the pseudo-valence charge with the norm-conserving plane-wave pseudopotential method [15] within the LDA framework [16, 17] for the electron exchange–correlation energy. We used pseudopotentials proposed by Troullier and Martins [18] with the separable approximation [19] and the partial-core correction [20]. To obtain the final converged wavefunction, the preconditioned conjugate gradient method [21] modified by Bylander *et al* [22] with the charge-mixing scheme given by Kerker [23], which has been shown to be suitable for large metallic systems [24], was used together with the Gaussian smearing technique [25]. The energy cut-off for the plane waves was set to 52.5 Ryd. The core charge density was described as the superposition of those of the atoms or ions, which were utilized in constructing the pseudopotentials.

The positron wavefunction was obtained in a similar way. It was expanded into a plane-wave basis set and refined with the preconditioned conjugate gradient method. For both LDA and GGA cases, we used the same electron–positron correlations and enhancement factors as were used in the SNA-FD calculations.

The calculations were made on (6, 0), (8, 0), (10, 0), (12, 0), (8, 8) and (10, 10) bundles with the inter-tube distance of 3.30 Å.

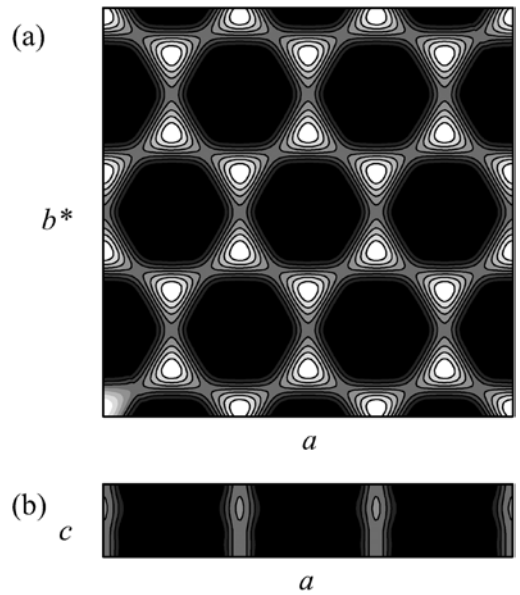


**Figure 1.** The positron density distribution in the (6, 0) SWNT bundle. The SNA-FD method and the LDA were used in the calculation. (a) A profile in the *ab*-plane perpendicular to the tube axis. One SWNT is located at the centre. The area shown is $24 \times 24$ Å$^2$. (b) A profile in the *ac*-plane along the tube axis. The inter-tube distance is 3.30 Å. The area shown is $24 \times 4.26$ Å$^2$.

## 3. Results and discussion

Figures 1–3 represent the positron distributions obtained with the SNA-FD method and the LDA in the (6, 0), (8, 0) and (10, 0) bundles, respectively. For the (6, 0) bundle, positrons are predominantly distributed in the interstitial region. On the other hand, for the (10, 0) bundle, positrons are almost confined into the inside of the SWNTs. As for the (8, 0) bundle, an intermediate situation is shown. For quantification, the positron density has been integrated inside the SWNT and its fraction against the total population has been evaluated for each bundle. The resultant values are plotted in figure 4 as a function of the SWNT diameter. It is shown that the positron density shifts from the interstitial region to the inside of the SWNTs when the SWNT diameter exceeds approximately twice the inter-tube distance (3.30 Å).

The calculated positron lifetimes are plotted in figure 5, correspondingly, as a function of the SWNT diameter. With the SWNT diameter increasing, the positron lifetime increases from 250 to 480 ps.

Figures 6 and 7 represent the values of the fraction and the positron lifetime obtained with the SNA-FD method and the LDA when the inter-tube distance is 3.15 Å. The qualitative behaviour is very similar to that shown in figures 4 and 5. The diameter at which there is a transition of the positron distribution from the interstitial region to the inside of the SWNTs shifts slightly to a lower value. For the (6, 0) and (7, 0) SWNT bundles, in which positrons are distributed in the interstitial region, the positron lifetime values decrease compared to those for the inter-tube distance of 3.30 Å. In contrast, the positron lifetimes for the (9, 0) and (10, 0) bundles do not show significant changes, since positrons are distributed in the inside of the SWNTs and the sizes of the SWNTs are kept constant.

The resultant values of the fraction and the positron lifetime for the GGA are shown in figures 8 and 9. The inter-tube distance is 3.30 Å. These results are quite different from those

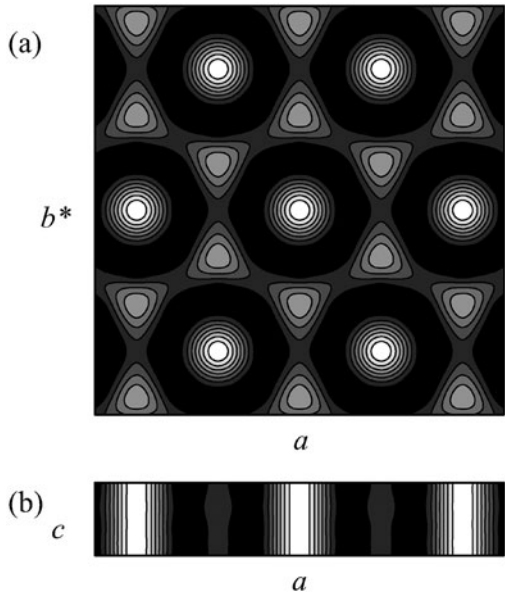


**Figure 2.** The positron density distribution in the (8, 0) SWNT bundle. The SNA-FD method and the LDA were used in the calculation. (a) A profile in the *ab*-plane perpendicular to the tube axis. One SWNT is located at the centre. The area shown is 24 × 24 Å$^2$. (b) A profile in the *ac*-plane along the tube axis. The inter-tube distance is 3.30 Å. The area shown is 24 × 4.26 Å$^2$.

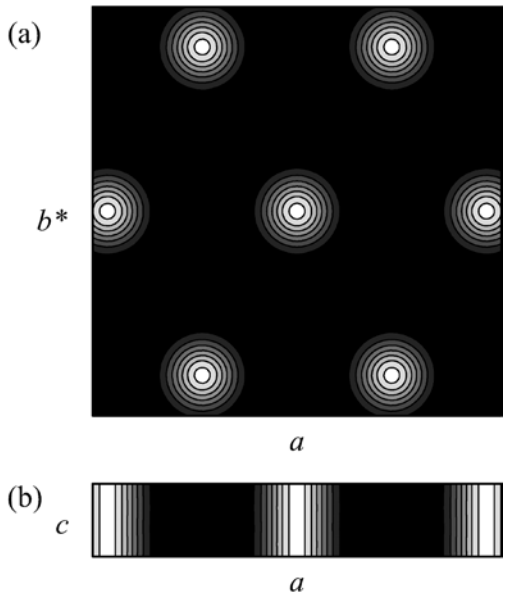


**Figure 3.** The positron density distribution in the (10, 0) SWNT bundle. The SNA-FD method and the LDA were used in the calculation. (a) A profile in the *ab*-plane perpendicular to the tube axis. One SWNT is located at the centre. The area shown is 24 × 24 Å$^2$. (b) A profile in the *ac*-plane along the tube axis. The inter-tube distance is 3.30 Å. The area shown is 24 × 4.26 Å$^2$.

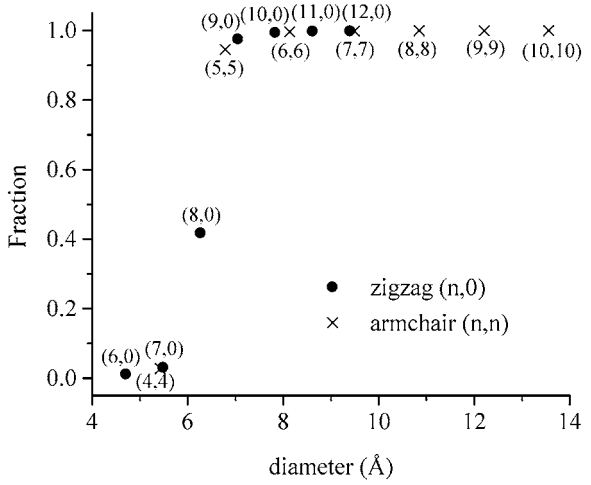


**Figure 4.** The fraction of the positron density distribution inside the SWNT as a function of the SWNT diameter. The SNA-FD method and the LDA were used in the calculation. The inter-tube distance is 3.30 Å.

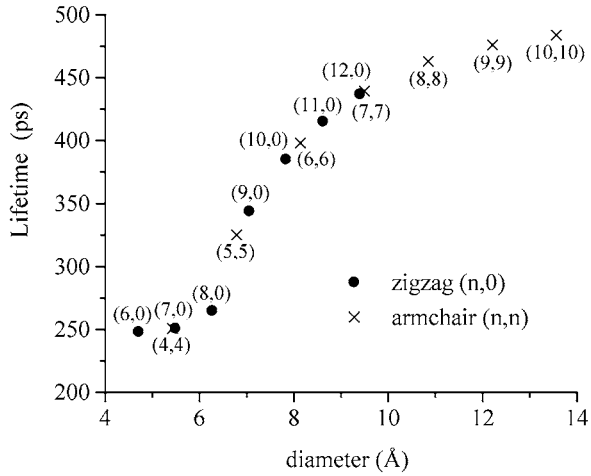


**Figure 5.** The positron lifetime in the SWNT bundles as a function of the SWNT diameter. The SNA-FD method and the LDA were used in the calculation. The inter-tube distance is 3.30 Å.

for the LDA shown in figures 4 and 5. Although the positron density shifts from the interstitial region to the inside of the SWNTs at a similar SWNT diameter to that for the LDA results, there is a second step. The positron density shifts to the interstitial region again when the SWNT diameter exceeds 10 Å. The positron lifetime increases with the SWNT diameter increasing up to ∼10 Å. The values and the change range are much larger than those for the LDA results. A sudden drop of the lifetime is found at around 10 Å. This corresponds to the second step in figure 8.

The results obtained with the *ab initio* method are shown in figures 10 and 11. The inter-tube distance is 3.30 Å. Both the LDA and the GGA results are plotted. As for the LDA results, positron lifetimes obtained with the *ab initio* method are very similar to those obtained with the SNA-FD method. The positron distribution shift occurs at a slightly larger diameter for

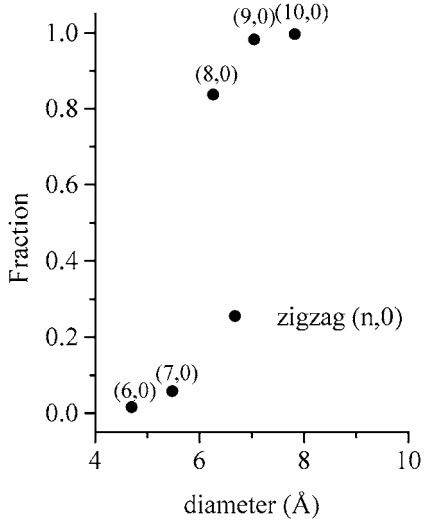


**Figure 6.** The fraction of the positron density distribution inside the SWNT as a function of the SWNT diameter. The SNA-FD method and the LDA were used in the calculation. The inter-tube distance is 3.15 Å.

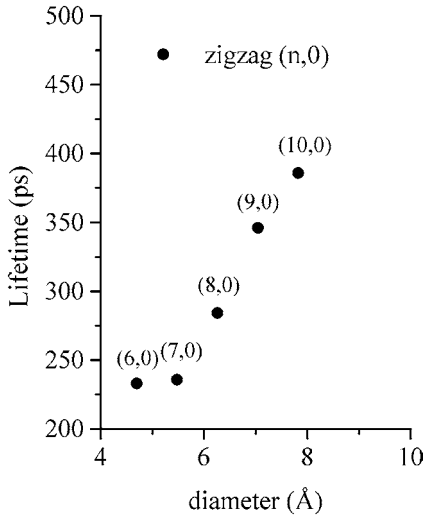


**Figure 7.** The positron lifetime in the SWNT bundles as a function of the SWNT diameter. The SNA-FD method and the LDA were used in the calculation. The inter-tube distance is 3.15 Å.

the *ab initio* case than for the SNA-FD case. In contrast, for the GGA results, there are large differences in positron distribution and lifetime between the two calculation methods. The positron distribution shift occurs only once at a larger diameter (12–14 Å) compared with the first shift for the SNA-FD method. As already mentioned in [9, 10], the GGA is much more sensitive to details of the electronic structure. The *ab initio* results would be more reliable than the SNA-FD ones.

For reference, in other carbon forms, positron lifetimes calculated with the SNA-FD method and the LDA were reported to be 90, 180 and 327 ps, for diamond, graphite and $C_{60}$,

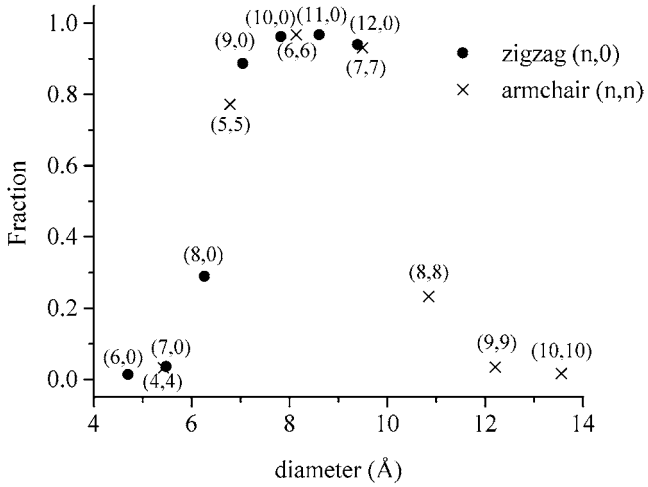


**Figure 8.** The fraction of the positron density distribution inside the SWNT as a function of the SWNT diameter. The SNA-FD method and the GGA were used in the calculation. The inter-tube distance is 3.30 Å.

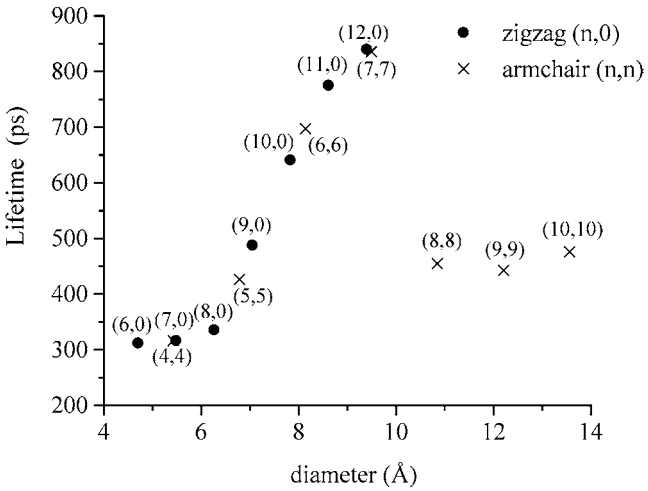


**Figure 9.** The positron lifetime in the SWNT bundles as a function of the SWNT diameter. The SNA-FD method and the GGA were used in the calculation. The inter-tube distance is 3.30 Å.

respectively [26, 27]. As compiled in [26], the experimental lifetimes are slightly longer than these values. The reason is that these materials are not good metals. Assuming semiconducting screening [28], better agreement can be obtained [26, 27]. As for the organic conductor tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ), we have found that adopting the GGA gives much better agreement in positron lifetime estimations than the LDA [29, 30]. The LDA and GGA lifetimes obtained with the *ab initio method* are 223 and 351 ps [30], respectively, while the experimental lifetime is 338 ps [29].

As far as the author is aware, positron lifetime measurements were performed only on MWNTs as mentioned above. It is not straightforward to compare the present results with the results on MWNTs. The experimentally obtained lifetimes range from 355 to 387 ps.

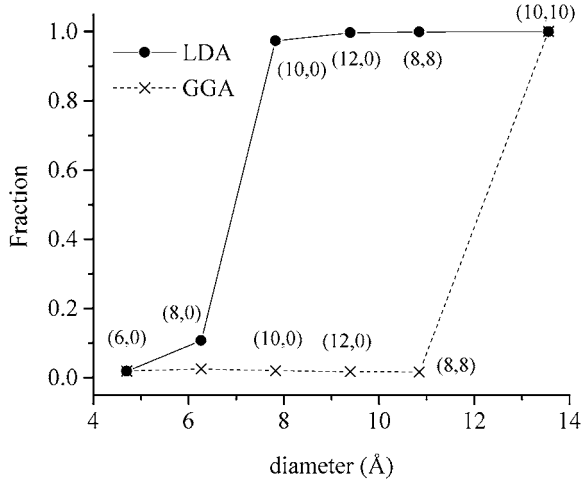


**Figure 10.** The fraction of the positron density distribution inside the SWNT as a function of the SWNT diameter. The *ab initio* method was used in the calculation. The inter-tube distance is 3.30 Å.

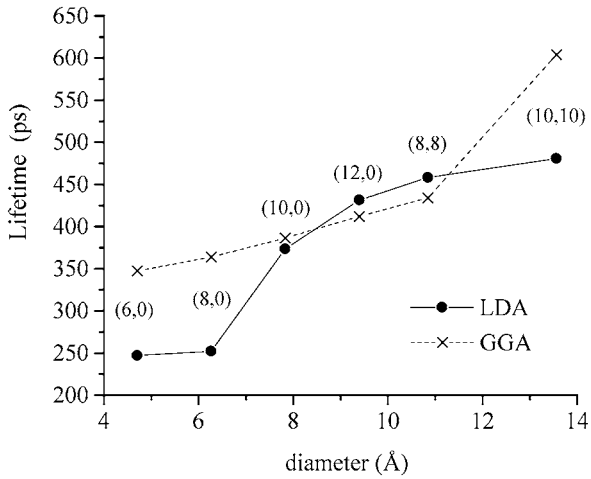


**Figure 11.** The positron lifetime in the SWNT bundles as a function of the SWNT diameter. The *ab initio* method was used in the calculation. The inter-tube distance is 3.30 Å.

If we rely on the LDA results, these lifetimes correspond to positron annihilation inside the (10, 0) SWNT. Considering that the LDA lifetime is usually underestimated, smaller SWNTs would be plausible. For smaller sizes of SWNT bundles, positrons tend to be distributed in the interstitial region, however. On the other hand, if we rely on the GGA results, these correspond to positron annihilation in the interstitial region of SWNT bundles with size between (7, 0) and (10, 0). These sizes are much smaller than those for MWNTs for the experiments. Thus, it is difficult to compare the present calculations with the experimental results. The experimentally observed lifetime was tentatively ascribed to annihilation at the MWNT surface [4, 5].

Although it is difficult to synthesize single-size SWNTs at present, the average size can be controlled. When considering solid surfaces, both the LDA and the GGA fail to describe the electron–positron correlation in the vacuum part [9, 10]. Perhaps they are not valid for very

sparse systems such as bundles of large-size SWNTs. Systematic work on SWNT bundles would be of great use to clarify the limit of their validity.

## 4. Conclusions

The positron density distributions and lifetimes for bundles of various sizes of SWNT have been calculated with different calculation methods (the SNA-FD method and the *ab initio* method) and approximations describing the electron–positron correlation (the LDA and the GGA). As for the calculations with the LDA, the SNA-FD and *ab initio* methods give similar results. Positrons are predominantly distributed in interstitial regions for smaller-size nanotubes while they are distributed inside nanotubes for larger sizes. The estimated positron lifetime ranges from 250 to 480 ps as a function of the nanotube diameter. In contrast, the GGA results are very sensitive to details of the electronic structure. The positron distributions and lifetimes obtained show quite different behaviours according to the two calculation methods. Systematic investigation of the positron state in different-size SWNT bundles is expected to provide useful information concerning the nature of electron–positron correlation.

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## References

[1] Iijima S 1991 *Nature* **354** 56
[2] Hamada N, Sawada S and Oshiyama A 1992 *Phys. Rev. Lett.* **68** 1579
[3] Thess A, Lee R, Nikolaev P, Dai H, Petit P, Robert J, Xu C, Lee Y H, Kim S G, Rinzler A G, Colbert D T, Scuseria G E, Tománek D, Fischer J E and Smalley R E 1996 *Science* **273** 483
[4] Ito Y and Suzuki T 1999 *Phys. Rev.* B **60** 15 636
[5] Fukutomi T, Murakami H and Sano M 2001 *Mtg Abstr. Phys. Soc. Japan* **56** 681
[6] Ohdaira T, Suzuki R, Kobayasi Y, Akahane T and Dai L 2002 *Appl. Surf. Sci.* **194** 291
[7] Puska M J and Nieminen R M 1983 *J. Phys. F: Met. Phys.* **13** 333
[8] Boroński E and Nieminen R M 1986 *Phys. Rev.* B **34** 3820
[9] Barbiellini B, Puska M J, Torsti T and Nieminen R M 1995 *Phys. Rev.* B **51** 7341
[10] Barbiellini B, Puska M J, Horhonen T, Harju A, Torsti T and Nieminen R M 1996 *Phys. Rev.* B **53** 16 201
[11] Kimball G E and Shortley G H 1934 *Phys. Rev.* **45** 815
[12] Brandt W and Rheinheimer J 1971 *Phys. Lett.* A **35** 109
[13] Saito R, Dresselhaus G and Dresselhaus M S 1998 *Physical Properties of Carbon Nanotubes* (London: Imperial College Press)
[14] Okada S, Oshiyama A and Saito S 2000 *Phys. Rev.* B **62** 7634
[15] Hamann D R, Schluter M and Chiang C 1979 *Phys. Rev. Lett.* **43** 1494
[16] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[17] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[18] Troullier N and Martins J L 1991 *Phys. Rev.* B **43** 1993
[19] Kleinman L and Bylander D M 1982 *Phys. Rev. Lett.* **48** 1425
[20] Louie S G, Froyen S and Cohen M L 1982 *Phys. Rev.* B **26** 1738
[21] Teter M P, Payne M C and Allan D C 1989 *Phys. Rev.* B **40** 12 255
[22] Bylander D M, Kleinman L and Lee S 1990 *Phys. Rev.* B **42** 1394
[23] Kerker G P 1981 *Phys. Rev.* B **23** 3082
[24] Kohyama M 1996 *Modell. Simul. Mater. Sci. Eng.* **4** 397
[25] Fu C-L and Ho K-M 1983 *Phys. Rev.* B **28** 5480

[26] Puska M J and Nieminen R M 1992 *J. Phys.: Condens. Matter* **4** L149
[27] Ishibashi S, Terada N, Tokumoto M, Kinoshita N and Ihara H 1992 *J. Phys.: Condens. Matter* **4** L169
[28] Puska M J, Mäkinen S, Manninen M and Nieminen R M 1989 *Phys. Rev.* B **39** 7666
[29] Ishibashi S, Tokumoto M, Kinoshita N, Terada N, Ihara H, Suzuki R, Ohdaira T, Mikado T and Anzai H 1996 *Can. J. Phys.* **74** 534
[30] Ishibashi S and Kohyama M 2000 *Radiat. Phys. Chem.* **58** 437