Electron-capture decay rate of $^7$Be@C$_{60}$ by first-principles calculations based on density functional theory

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Carrying out a first-principles calculation assuming linear relationship between the electron density at Be nucleus and the electron-capture (EC) decay rate, we explained why $^7$Be@C$_{60}$ shows higher EC decay rate than $^7$Be crystal, which was originally found experimentally by Ohtsuki et al. [Phys. Rev. Lett. 93, 112501 (2004)]. From the results of the calculation, we found that there are inequivalent four stable (i.e., lower energy) Be sites inside C$_{60}$ and that center of C$_{60}$ (C$_{C_{60}}$) is the most favorable site. For C$_{C_{60}}$, the electron density at the Be nucleus is the highest. It is also much higher than that at the Be nucleus in a Be crystal. Also, we estimated the expected electron density at the Be nucleus at room temperature by taking statistical average of the electron densities at the four Be nucleus sites using the Boltzmann distribution. The results of the calculation show fairly good agreement with the experimental results. In this paper, we focus on the detail of calculation, which was not fully demonstrated in the paper by Ohtsuki.

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I. INTRODUCTION

Since Kroto et al. discovered the C$_{60}$ molecule, many scientists have been interested in the novel properties of this new material. One of the most attractive features is that C$_{60}$ can encapsulate another atom. It is interesting to study the new properties of the cluster, M@C$_{60}$, and how the atom behaves inside C$_{60}$. So far, many works have been devoted to this subject.$^2$–$^10$

Recently, Ohtsuki et al. measured the electron-capture (EC) decay rate of the $^7$Be nucleus inserted inside the C$_{60}$ cage.$^9$,$^{10}$ The EC decay reaction can be written as

$$p + e^- \rightarrow n + \nu_e,$$  \hspace{1cm} (1)

where $p$, $e^-$, $n$, and $\nu_e$ are proton, electron, neutron, and neutrino, respectively. A $^7$Be atom decays to $^7$Li by electron capture (EC). As first suggested by Segré et al.,$^{11}$–$^{13}$ the EC decay rate depends on the density of atomic electrons at the nuclear site. Assuming a linear relation between decay rate and electron density, we expect that the EC decay rate is proportional to the electron density at the Be nucleus. External factors such as chemical forms and pressure may alter the electron density at the nucleus and thus affect the EC decay rate. In recent studies, there have been several observations or calculations concerning the change in half-life according to the host materials,$^{14}$–$^{18}$ chemical forms,$^{19}$–$^{22}$ and pressure.$^{23}$,$^{24}$ Although, in most of these environments, the half-life is longer than 53.10 days, Ohtsuki et al. found that the half-life of $^7$Be@C$_{60}$ is 52.65 ± 0.04 days at room temperature (RT) (293 K) and moreover 52.47 ± 0.04 days at liquid-helium temperature (5 K).$^9$,$^{10}$ This result shows that the chemical environment inside C$_{60}$ drastically changes the electronic density at the Be nucleus and that the temperature may also affect the electronic density at the Be nucleus. In this paper, we discuss the EC decay rate of $^7$Be@C$_{60}$ by carrying out a first-principles calculation for the electronic density at the Be nucleus inside C$_{60}$ on the basis of the density functional theory (DFT).

II. CALCULATION METHOD

In order to express correctly the cusp-like profile of the electron density near the nucleus, we use the all-electron first-principles calculation program, DMol$^3$. In a linear combination of the atomic orbital (LCAO) method and the numerical localized orbitals as basis functions. This basis set is appropriate for expressing such cusp-like profile of the electron density near the nucleus. For the exchange-correlation energy, we employed the BLYP method, which combines the exchange functional due to Becke$^{25}$ with the correlation functional of Lee-Yang-Parr.$^{28}$ In DMol$^3$, basis functions are given numerically as values on an atomic-centered spherical-polar mesh, rather than as analytical functions (e.g., Gaussian orbitals). The angular portion of each
function is the appropriate spherical harmonic functions. The radial portion is obtained by solving the atomic DFT equations numerically. Therefore, even only one function has important information in numerical basis set, while only one function in analytical basis set has less meaning as an atomic orbital. In the present work, we used the double-numeric quality basis set with polarization functions \( \text{H}_20849 \text{DNP} \). The size of the DNP basis set is comparable to Gaussian 6–31G** basis set. However, the numerical basis set is much more accurate than a Gaussian basis set of the same size as demonstrated above.

III. RESULTS AND DISCUSSION

A. Be@C\(_{60}\) at 0 K

At first, we explored the most stable sites of Be in a C\(_{60}\) cage. For this purpose, we carried out single point energy calculations varying the Be site on a high symmetry plane inside C\(_{60}\). C\(_{60}\) has the point group, \( \text{I}_h \), i.e., the full icosahedral symmetry, which has 120 point-group operations. In Fig. 1, an irreducible region of \( \text{I}_h \) in C\(_{60}\) is shown. High symmetric triangles constructing this region except surface of C\(_{60}\) can be unfolded into one sheet of plane across high symmetric points such as the center of C\(_{60}\), the centers of five- and six-membered rings, and the centers of single and double bonds. So, the calculations were done for the 962 Be sites, which are grid points on that plane. We excluded points outside C\(_{60}\) and those which are too close to carbon atom, i.e., less than 0.5 Å.

Total energies calculated for those Be sites are plotted to draw a contour map of the potential energy that Be atom feels in Fig. 2. From this result, we see that there are inequivalent five points as candidates for local minima of Be sites: center of C\(_{60}\) (C\(_{C\text{60}}\)), under the center of a five-membered ring (U\(_5\)), under the center of a six-membered ring (U\(_6\)), and under the center of a double bond (U\(_db\)), respectively. Each point is also shown in Fig. 1.

The geometry of C\(_{60}\) was then optimized for the five stable sites (C\(_{C\text{60}}\), U\(_5\), U\(_6\), U\(_sb\), and U\(_db\)) to make sure whether those five Be sites are really stable. The results are shown in Table I. A part of the data presented in Table I is taken from our previous paper.\(^{10}\) From Table I, one can see that the most stable position of the Be atom inside the C\(_{60}\) cage is C\(_{C\text{60}}\) among all the cases investigated in the present

<table>
<thead>
<tr>
<th>Total energy difference (eV)</th>
<th>Spin magnetic moment (( \mu_B ))</th>
<th>Electron density at Be nucleus (e(^{-}/a_B^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{C\text{60}})</td>
<td>0.000</td>
<td>36.016</td>
</tr>
<tr>
<td>U(_sb)</td>
<td>0.098</td>
<td>35.243</td>
</tr>
<tr>
<td>U(_5)</td>
<td>0.068</td>
<td>35.287</td>
</tr>
<tr>
<td>U(_6)</td>
<td>0.142</td>
<td>35.332</td>
</tr>
<tr>
<td>U(_db)</td>
<td>0.309</td>
<td>35.377</td>
</tr>
<tr>
<td>Be atom</td>
<td>0.0</td>
<td>35.954</td>
</tr>
<tr>
<td>Be crystal</td>
<td>0.0</td>
<td>35.423</td>
</tr>
</tbody>
</table>
calculation. For U_5, U_6, and U_db sites, the system shows 2.0 \( \mu_B \) spin magnetic moment. U_db shows very large total energy compared to other sites, so we decide to discard it from the candidates.

We plot the highest occupied molecular orbital (HOMO) for each Be site in Fig. 3 to see the difference in the electronic structure among these four Be sites except U_db. Since we already posted this figure in the previous report,\(^{10}\) we discuss this briefly here. From this figure, we can see that only the case of C_C60 has an orbital localized around the Be atom just like an isolated atom. For the case of U_sb, the Be2s and \( t_{1u} \) [the lowest unoccupied molecular orbital (LUMO) of C60] form bonding and antibonding orbitals. The bonding orbital and the antibonding orbitals become HOMO and LUMO, respectively. For U_5 and U_6 sites, HOMO and the second highest occupied molecular orbital (HOMO-1) have the same spin direction. In these two cases, Be atom is close to a five- or six-membered ring, and one of the Be2s electrons moves to \( t_{1u} \), flipping the spin direction. Since one electron at the HOMO level, i.e., \( t_{1u} \), spreads over a large area of C60 while the other electron remaining at the Be2s state is confined only in a small region around Be atom, there is an energy gain by the triplet spin configuration due to the exchange interaction.

As side products of these geometry optimizations, we could obtain the electron density at each Be nucleus site. In addition to the inequivalent four Be sites inside C60, we carried out the all-electron calculation also for a free Be atom and for Be metal to determine their electron densities at the Be nucleus. For Be metal, we carried out structural optimization also. The Be crystal is hexagonal and two Be atoms exist in a primitive unit cell. In the optimization, we took \( 18 \times 18 \times 12 \) \( k \) points. The results of the electron density at the Be nucleus for all these systems are also shown in Table I. Among all these results, C_C60 has the largest value. It is even larger than that of a free Be atom. This is because the Be2s electrons are closely confined in C60 and have higher amplitude at the Be nucleus. If we compare the density at the other three sites of Be inside C60 (except for C_C60) and in the Be metal, we find that the density is higher in the Be metal than at the other three sites inside C60. In the Be metal, the tails of Be2s electrons spread from the adjacent Be atoms are superposed at the Be nucleus. In contrast, there is only one Be atom in U_5, U_6, and U_sb, and the Be2s electrons spread into whole C60. Since there is no overlap from other Be2s electrons like the Be metal, the electron density at U_5, U_6, and U_sb is less than that in the Be metal.

To confirm the charge transfer, we plotted the difference in the electronic charge distribution for U_5, C_C60, and Be metal. The differences in the charge density distributions are defined here by

\[
\rho_{\text{diff}}(r) = \rho_{\text{Be@C}_60}(r) - [\rho_{\text{C}_60}(r) + \rho_{\text{Be, atom}}(r)]
\]

or,

\[
\rho_{\text{diff}}(r) = \rho_{\text{Be, metal}}(r) - \rho_{\text{Be, atom}}(r),
\]

where \( \rho_{\text{C}_60}(r) \), \( \rho_{\text{Be, atom}}(r) \), \( \rho_{\text{Be@C}_60}(r) \), and \( \rho_{\text{Be, metal}}(r) \) are the electronic charge densities at \( r \) for C60, free Be atom, Be@C60, and Be metal, respectively.

In Fig. 4, the \( \rho_{\text{diff}}(r) \) is shown in color. For the case of Be@C60, the red or blue regions show the areas in which electronic charge density increases or decreases, respectively, compared to the charge density given by the superposition of a Be atom and C60. As for the Be metal, the red or blue regions have almost the same meaning as those of Be@C60, but the comparison is done against the charge density given by the superposition of Be atoms. From this figure, we can easily make sure that the charge density at the Be nucleus of C_C60 is larger than that of a free Be atom. On the contrary, for the cases of Be metal and U_5, it is clear that the electronic charge around the Be nucleus goes outside and the density at the Be nucleus decreases.

Figure 5 shows experimentally measured half-lives of the EC decay for several systems.\(^{10}\) According to these experimental results, one can see that the EC decay rate of \(^{7}\)Be@C60 at 5 K is the fastest. This experimental result suggests that \(^{7}\)Be@C60 at 5 K has the largest electron density at Be nucleus. This is certainly consistent with the present (computational) result telling that C_C60 is the most stable.
Be site inside C\textsubscript{60} at the absolute zero temperature and its electron density at the Be nucleus is the largest among four low-energy Be sites inside C\textsubscript{60}.

### B. Be@C\textsubscript{60} at room temperature

As we mentioned above, the EC decay rate of \textsuperscript{7}Be@C\textsubscript{60} is higher at 5 K than at RT. We showed C\textsubscript{60} is the most preferable Be position at 0 K in Sec. III A. At RT, Be atoms perform ratchet motion among stable Be sites inside C\textsubscript{60}. Although energy barrier from C\textsubscript{C60} to other sites may be high to pass through, the hopping should occur during a very long time scale of real measurement such as more than 160 days in the experiment.\textsuperscript{10} Here, we estimate the probability of finding a Be atom at each site at RT by assuming the Boltzmann distribution and estimate the expected electron density at the Be nucleus at RT by taking the statistical average of the electron densities at different Be positions. That is, using the total energy \( E(r) \) and the electron density \( \rho(r) \) calculated at each Be position \( r \) inside the C\textsubscript{60} cage, we can evaluate the statistical average of the electron density at the Be nucleus at temperature \( T \) according to the Boltzmann distribution with the Be nucleus position \( r \) as follows:

\[
\langle \rho(r) \rangle = \frac{\int \rho(r) \exp \left( - \frac{E(r)}{k_B T} \right) dr}{\int \exp \left( - \frac{E(r)}{k_B T} \right) dr}.
\]

Here, \( k_B \) is the Boltzmann constant. Expanding \( E(r) \) around each local minimum position \( r_i = (x_i, y_i, z_i) \) in a quadratic form as

\[
E(r) \sim E(r_i) + a_1(x-x_i)^2 + a_2(y-y_i)^2 + a_3(z-z_i)^2
\]

we readily evaluate the local integration around \( r_i \) to be

\[
\int_{\text{around } r_i} \exp \left( - \frac{E(r)}{k_B T} \right) dr \sim \frac{(\pi k_B T)^{3/2}}{a_1 a_2 a_3^{3/2}} \exp \left[ - \frac{E(r_i)}{k_B T} \right].
\]

Moreover, we write the number of equivalent positions as \( \alpha_i \). Since C\textsubscript{60} is highly symmetric (with the I\textsubscript{h} symmetry), there are \( \alpha_i = 20, 12, \) and 30 equivalent positions for U\textsubscript{6} (\( i = 2 \)), U\textsubscript{5} (\( i = 3 \)), and U\textsubscript{sb} (\( i = 4 \)), respectively. (Obviously \( \alpha_1 = 1 \) at C\textsubscript{C60}. Therefore the expression for the average density is given by

\[
\langle \rho(r) \rangle \sim \sum_{i=1}^{4} \frac{\alpha_i}{\alpha_i a_1 a_2 a_3^{3/2}} \exp \left[ - \frac{E(r_i)}{k_B T} \right].
\]

In reality, due to the asymmetry, the coefficients of the plus and minus directions for quadratic form of \( E(r) \) are different, and a slight modification of Eq. (6) is necessary. Consequently, the final expression for the average density at finite temperature is given by
where \( l, m, \) and \( n \), which are 1 or 2, represent plus or minus direction of \( x, y, \) and \( z \), respectively. To obtain the potential coefficients around each local minimum position, i.e., \( a_+, b_+, c_+ \), total energies of \( \text{Be} @ \text{C}_{60} \) were calculated, changing Be positions little by little (0.05 Å each) and plotted and fitted in quadratic functions. In these calculations, each system was rotated so that the line across the center of \( \text{C}_{60} \) and each local minimum is along \( z \) axis. The total energies and the fitted quadratic functions around each local minimum position are shown in Fig. 6. The obtained potential coefficients are listed in Table II. In the graphs of Fig. 6, the energy corresponding to RT (1 eV=11600 K) is expressed as a horizontal line, and each quadratic curve crosses this line at short distance, which is less than 0.2 Å except \( \text{C}_-\text{C}_{60} \). This implies that the energies of transition states from one site to other sites are quite high for Be to pass through at RT within a short time and Be may stay around one site for a long time at RT in thermal equilibrium state.

At absolute zero temperature (\( T=0 \)), the Be atom is located at \( \text{C}_-\text{C}_{60} \) and the electron density at the Be nucleus is equal to 36.016 \( e^-/a_B^3 \), while at the room temperature, it is estimated to be 35.899 \( e^-/a_B^3 \) from Eq. (7). Here, \( a_B \) denotes the Bohr radius. The relative difference between them amounts to 0.33%, which should be compared with the relative difference 0.34% of the experimentally determined half-
C60 at absolute zero temperature is about 1.67% faster than 53.25/H20849 more precise temperature dependence time scales into account, and thermal equilibrium would be In the present study, we should take very long experimental K, 60 K, etc. is surprisingly a very big change in the half-life.ing to the present calculation, the EC decay rate of7Be in 7Be in Be metal at absolute zero temperature, which that of 7Be crystal, which was originally found experimentally by Ohtsuki et al.9,10 We found that there are inequivalent four stable Be sites inside C60 and that center of C60 (C_C60) is the most favorable site. For C_C60, we showed that the electron density at the Be nucleus is the highest among these Be sites and also higher than Be metal. Since valence electrons of Be are closely confined inside C60, the electron density at the Be nucleus has a relatively large value for C_C60. Also, we estimated expected electron density at the Be nucleus at room temperature by statistical calculation including total energies and the electron densities at various Be nucleus positions. The results of our calculation are in fairly good agreement with the experimental results. By means of the method adopted here, it is basically possible to calculate theoretically the “averaged” electron density at the 7Be nucleus at any temperature. That is, we succeeded in representing the temperature dependence of the averaged electron density at the 7Be nucleus by analytical formula using the Boltzmann distribution with Be position. In the present study, we should take very long experimental time scales into account, and thermal equilibrium would be totally achieved. It is intriguing to investigate experimentally more precise temperature dependence (e.g., at T=20 K, 40 K, 60 K, etc.) of the EC decay rate. Such an investigation is, however, left for a future study.

IV. CONCLUSION

In this paper, we have explained by means of a first-principles calculation why 7Be@C60 shows a higher EC decay rate than 7Be crystal, which was originally found experimentally by Ohtsuki et al.9,10 We found that there are inequivalent four stable Be sites inside C60 and that center of C60 (C_C60) is the most favorable site. For C_C60, we showed that the electron density at the Be nucleus is the highest among these Be sites and also higher than Be metal. Since valence electrons of Be are closely confined inside C60, the electron density at the Be nucleus has a relatively large value for C_C60. Also, we estimated expected electron density at the Be nucleus at room temperature by statistical calculation including total energies and the electron densities at various Be nucleus positions. The results of our calculation are in fairly good agreement with the experimental results.

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TABLE II. Potential coefficients (eV/Å²), which are derived from the total energy calculation, changing the Be location from each stable point slightly to positive and negative directions along each Cartesian coordinate axis.

<table>
<thead>
<tr>
<th>Potential coefficients</th>
<th>(eV/Å²)</th>
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<tbody>
<tr>
<td>a_{i+}</td>
<td>0.545</td>
</tr>
<tr>
<td>a_{i-}</td>
<td>0.545</td>
</tr>
<tr>
<td>b_{i+}</td>
<td>0.545</td>
</tr>
<tr>
<td>b_{i-}</td>
<td>0.545</td>
</tr>
<tr>
<td>c_{i+}</td>
<td>0.545</td>
</tr>
<tr>
<td>c_{i-}</td>
<td>0.545</td>
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</tbody>
</table>

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</thead>
<tbody>
<tr>
<td>U_{c60}</td>
<td>0.545</td>
<td>0.545</td>
<td>0.545</td>
<td>0.545</td>
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</tr>
<tr>
<td>U_6</td>
<td>1.773</td>
<td>1.657</td>
<td>1.081</td>
<td>1.074</td>
<td>3.752</td>
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<tr>
<td>U_5</td>
<td>1.891</td>
<td>1.982</td>
<td>1.836</td>
<td>1.689</td>
<td>6.740</td>
<td>2.365</td>
</tr>
<tr>
<td>U_{sb}</td>
<td>0.843</td>
<td>1.195</td>
<td>1.921</td>
<td>1.921</td>
<td>8.765</td>
<td>6.431</td>
</tr>
</tbody>
</table>

lives (52.47 ± 0.04 days at liquid-helium temperature and 52.65 ± 0.04 days at room temperature). On the other hand, if we compare the electron density of Be@C60 at RT (35.899 e^-/a_0^3) with that of Be metal at absolute zero temperature (35.423 e^-/a_0^3), the relative difference between them amounts to 1.3%. This value should be compared with the relative difference 1.1% of the experimentally determined half-lives (52.65 ± 0.04 days for 7Be@C60 and 53.25 ± 0.04 days for Be metal at RT). The agreement between the theory and the experiment is fairly good. Accord-

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