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# Diamagnetic Currents in the Neutral He Atoms

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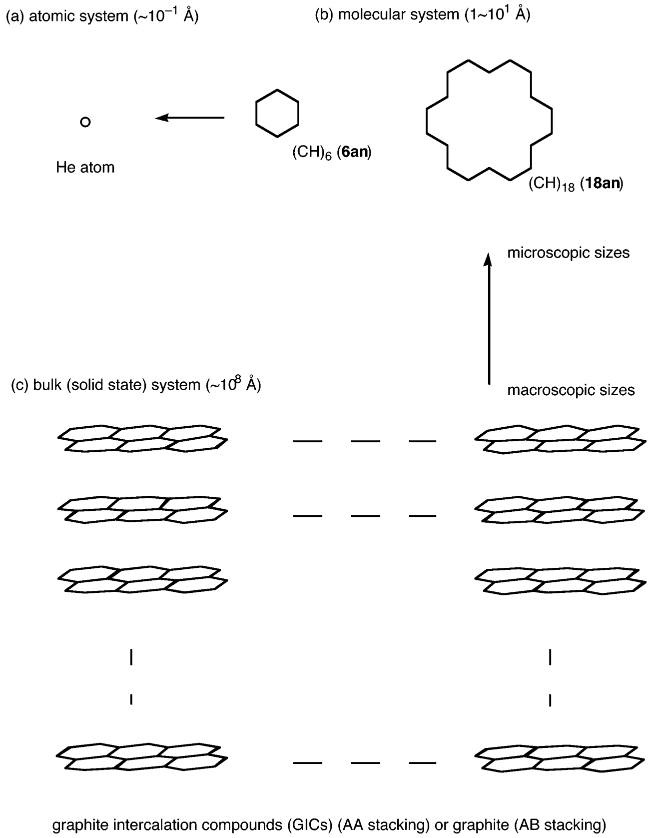
The mechanism of the occurrence of intraatomic diamagnetic currents in the neutral He atoms with microscopic sizes is investigated. It is found that most of all electrons can form electron pairs originating from attractive Coulomb interactions between two electrons with opposite spins occupying the 1s atomic orbital in the neutral He atom at 298 K. Intraatomic diamagnetic currents in the neutral He atoms with microscopic sizes can be explained by such electron pairing. The transition temperature $T_c^{\mathrm{He,1s}}$ value at which intraatomic diamagnetic currents can disappear in each He atom is estimated. The $T_c^{\mathrm{He,1s}}$ values for the neutral He atoms with microscopic sizes are estimated to be much larger than the superconducting transition temperatures $T_{\mathrm{c,BCS}}$ values for the conventional superconductors with macroscopic sizes. This result can be understood from continuous energy levels of electronic states in conventional superconductivity with macroscopic sizes, and from discrete energy levels of electronic states in the neutral He atoms with microscopic sizes. The energy difference between the occupied and unoccupied orbitals decreases with an increase in material size and thus the second-order perturbation effect becomes more important with an increase in material size. Therefore, the mechanism of the occurrence of intraatomic diamagnetic current in the neutral He atoms suggested in this research would not be true for materials with large sizes. The dependence of electronic properties on temperature in the diamagnetic currents in the neutral He atoms with microscopic sizes is studied and compared with that in the conventional superconductivity with macroscopic sizes.

## Introduction

London successfully developed the application of molecular orbital theory to the study of magnetic properties in 1937.[1] Modified secular equations in the presence of an external magnetic field, in particular, the important magnetic property of aromatic molecules associated with the existence of ring currents, were developed by Pople.[2−4] It is well-known that the diamagnetic anisotropy of aromatic hydrocarbons such as annulenes can be attributed to the induced ring currents in their $\pi$-electronic systems.[5,6] The diamagnetic ring currents of aromatic molecules such as $(CH)_6$ (**6an**) and $(CH)_{18}$ (**18an**) (Scheme 1b) are nondissipative currents similar in many respects to the persistent currents of superconducting rings and have been often referred to as a form of superconductivity.[1,7−9] However, it has been considered that the supercurrent of these molecules is not the same as the superconductivity of bulk materials. The relationship between the ring current and the virtual superconducting state in these molecular systems has been discussed.[10,11]

In the previous work, we provided an explanation of the diamagnetic ring current[12] in aromatic hydrocarbons with small molecular sizes, annulenes, such as **6an** and **18an**. By comparing these results in small molecular sizes, annulenes, such as **6an** and **18an**, with those in the macroscopic Bardeen−Cooper−Schrieffer (BCS)-type[13,14] conventional superconductors, we discuss how the size differences can have influence on the characteristics of electrical conducting (Scheme 1b,c). We showed that Coulomb interactions rather than electron−phonon interactions[15−17] play an essential role in the occurrence of ring current in small aromatic annulenes such as **6an** and **18an**. We

**SCHEME 1: Dependence of the Electronic Properties on Material Sizes**



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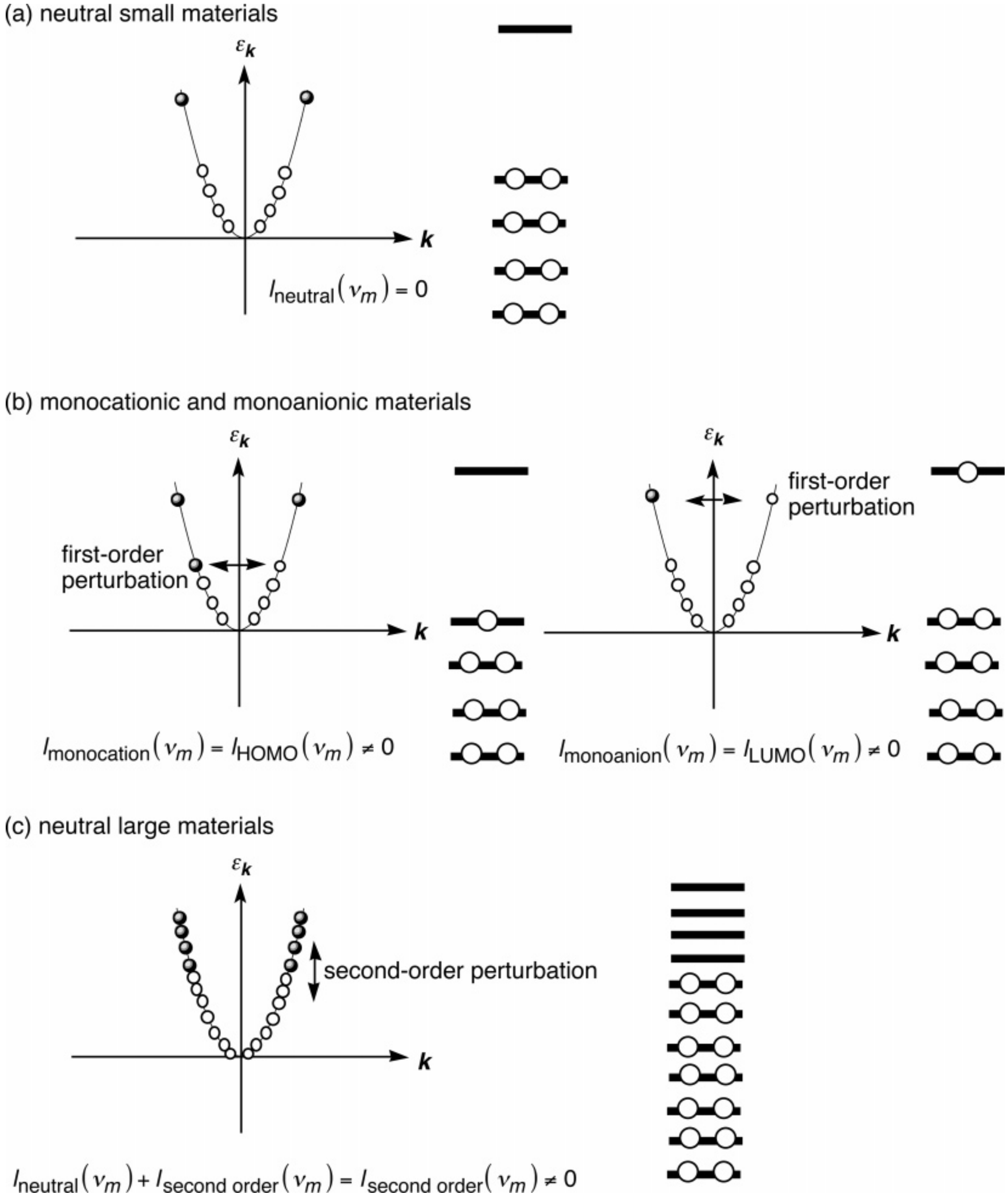

**Figure 1.** Momentum states and energy levels of electrons. Open circles on the parabolic curve represent energy levels occupied by an electron, and shaded circles represent energy levels not occupied by electrons.

also analyzed the critical temperature $T_c$ at which supercurrents completely disappear for conventional superconductors with macroscopic sizes and for aromatic annulenes with microscopic sizes such as **6an** and **18an**.

Diamagnetism in atomic systems such as He atoms (Scheme 1a) has been widely studied.[18] The intraatomic diamagnetic currents in the neutral He atoms are also nondissipative currents. However, there is no explanation of the mechanism of the occurrence of the intraatomic diamagnetic currents in the neutral He atoms from the point of view of solid-state physics and chemistry, as far as we know. It is natural to consider that the fundamental theory in solid-state physics and chemistry should be also applicable to the explanation of the fundamental electronic properties in one atomic system such as neutral He atoms with the size on the order of $10^{-1}$ Å (Scheme 1a) as well as in single molecules with sizes on the order of 1−10 Å, such as **6an** and **18an** (Scheme 1b). However, as will be discussed in the next sections, it is very difficult to explain the mechanism of the occurrence of intraatomic diamagnetic currents in the neutral He atoms from the point of view of the mechanism of the occurrence of normal metals with macroscopic sizes. Therefore, another new mechanism of the occurrence of intraatomic diamagnetic current in the neutral He atoms with microscopic sizes should be investigated.

In this research, we look into more microscopic material (i.e., one atomic system (size $10^{-1}$ Å)) (Scheme 1a) than in previous research (i.e., bulk system (size $10^{8}$ Å) or one molecular system (size 1−10 Å)) (Scheme 1b). We provide an explanation of the intraatomic diamagnetic current in the neutral He atom with microscopic size. By comparing these results in the microscopic neutral He atom (Scheme 1a) with those in the macroscopic BCS-type[13,14] conventional superconductors (Scheme 1c), we discuss how the size differences can have influence on the characteristics of electrical conducting (Scheme 1). We will show that Coulomb interactions play an essential role in the occurrence of intraatomic diamagnetic current in the neutral He atoms. We will also analyze the critical temperature $T_c$ at which diamagnetic currents disappear for conventional superconductors

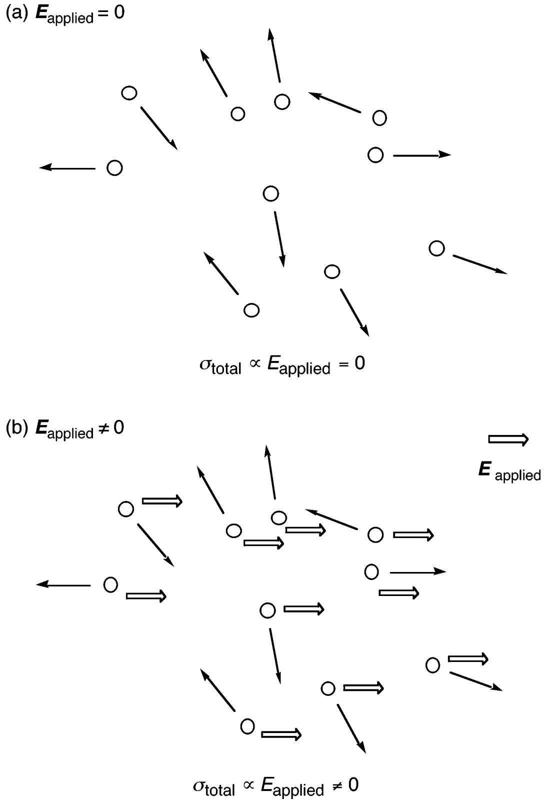

**Figure 2.** The motion of each electron (a) in no external applied electric field, and (b) in external applied electric field. Circles represent each electron. Small arrows indicate the direction of the momentum of each electron, and large arrows indicate the direction of the applied electric field.

with macroscopic sizes ($T_{\text{c,BCS}}$) and for the neutral He atoms with microscopic sizes ($T_{\text{c}}^{\text{He,1s}}$).

## Relationship between the Total Momentum States and the Electrical Conductivity

In this section, let us first discuss the electrical conductivity in view of electron−phonon interactions. That is, we discuss the conditions under which the electrical conductivity occurs in various electron configurations. Electron configurations and the electron−phonon interactions in various electronic states are illustrated in Figure 1.

Let us discuss the electrical conductivity from microscopic point of view. The motion of each electron is shown in Figure 2. When no external electric or magnetic field is applied, each electron moves randomly, according to the rule of solid-state physics (Figure 2a). On the other hand, the total momentum of all electrons must be zero when no external electric or magnetic field is applied ($\sigma_{\text{total}} = 0$), as shown in Figure 2a. This can be understood from the fact that we cannot expect the spontaneous net charge transfer to any direction without external applied electric or magnetic field. If an external electric or magnetic field is applied, the direction and magnitude of the total momentum states of all electrons should be changed according to such applied external electric or magnetic field, so the net charge transfer to the direction parallel to the applied external electric field can occur ($\sigma_{\text{total}} \neq 0$) (Figure 2b). Such changing ability of direction and magnitude of the total momentum states of all electrons depends on the electron configurations, as will be discussed below.

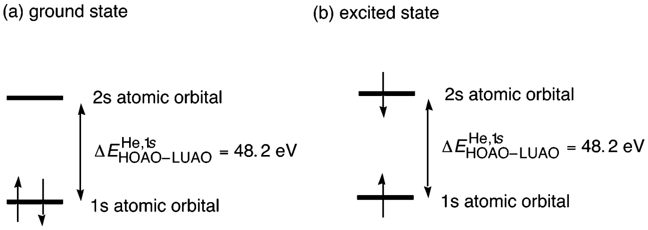

**Figure 3.** Energy levels of atomic orbitals and the ground and excited states in the neutral He atom.

Let us next look into the conditions under which the electrical conductivity can occur in various materials. First, large orbital overlap between two atoms and between two neighboring molecules are needed so the hopping ability of electrons to the neighboring atoms and molecules becomes effective. Second, the total momentum states of electrons should be efficiently changed by applied electric fields, according to solid-state physics. To realize the first condition, the distances between two neighboring atoms and between two neighboring molecules should not be large. Let us next look into the second condition. Here, we consider a one-electron approximation; the vibronic coupling constants of the vibronically active modes to the electronic states are defined as a sum of orbital vibronic coupling constants from all the occupied orbitals.[15]

$$g_{\text{electronic state}}(\nu_m) = \sum_{j}^{\text{occupied}} g_j(\nu_m) \tag{1}$$

Considering the one-electron approximation and that the first derivatives of the total energy vanish in the ground state at the equilibrium structure in neutral molecules, total electron−phonon coupling constant for the neutral molecule is zero (Figure 1a).

$$g_{\text{neutral}}(\nu_m) = \sum_{j}^{\text{HOMO}} g_{\text{j}}(\nu_m) = 0 \tag{2}$$

$$l_{\text{neutral}} = \sum_m h\upsilon_m g_{\text{neutral}}{}^2(\nu_m) = 0 \tag{3}$$

Let us look into the monocations and monoanions in which the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) are partially occupied by a hole and an electron, respectively. The $l_{\text{electronic state}}$ values for the monocations and monoanions can be defined by using the orbital vibronic coupling constants for the HOMO ($g_{\text{HOMO}}(\nu_m)$) and LUMO ($g_{\text{LUMO}}(\nu_m)$) (Figure 1b),[12,17]

$$l_{\text{monocation}} = l_{\text{HOMO}} = \sum_m h\upsilon_m g_{\text{HOMO}}{}^2(\nu_m) \neq 0 \tag{4}$$

for the monocations,

$$l_{\text{monoanion}} = l_{\text{LUMO}} = \sum_m h\upsilon_m g_{\text{LUMO}}{}^2(\nu_m) \neq 0 \tag{5}$$

for the monoanions. Negatively and positively charged benzene and [18]annulene, and graphite intercalation compounds (GICs), belong to such cases (Scheme 1b,c).

If the LUMO or HOMO is partially occupied by an electron or a hole, $l_{\text{electronic state}}$ values originating from the first-order perturbation are not zero (Figure 1b), and furthermore, the second-order perturbation effects become more important with an increase in material size. Furthermore, in such a case, the total momentum states of electrons can be easily changed continuously by even a small electric field, and thus the electrical

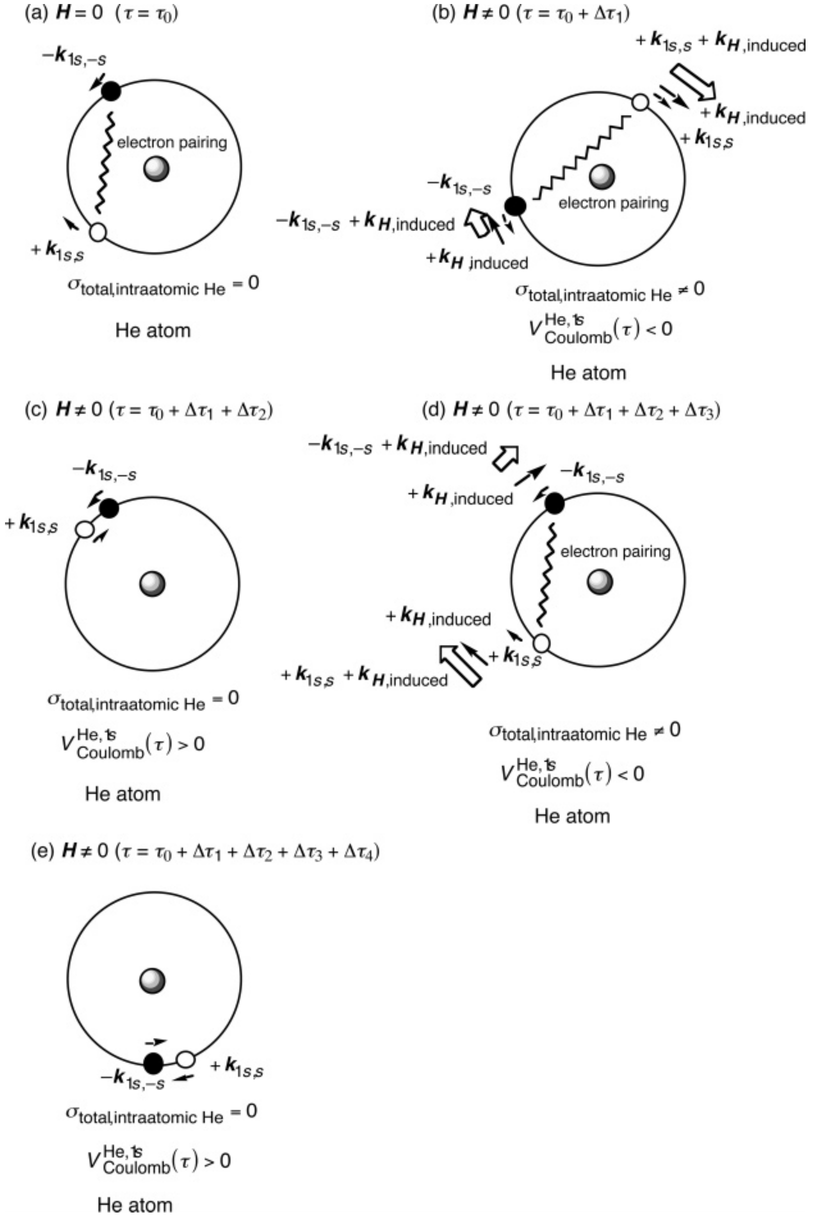

**Figure 4.** Electrical conductivity of electrons occupying the 1s atomic orbital in the neutral He atom. Opened and closed circles represent electrons moving around the nucleus, represented by shaded circles, clockwise and counter-clockwise, respectively. (a) $\mathbf{H} = 0$ $(\tau = \tau_0)$; the distance between two electrons is enough large and thus the Coulomb interactions between them are attractive. (b) $\mathbf{H} \neq 0$ $(\tau = \tau_0 + \Delta\tau_1)$; the distance between two electrons is enough large and thus the Coulomb interactions between them are attractive. (c) $\mathbf{H} \neq 0$ $(\tau = \tau_0 + \Delta\tau_1 + \Delta\tau_2)$; the distance between two electrons is very small and thus the Coulomb interactions between them are repulsive. (d) $\mathbf{H} \neq 0$ $(\tau = \tau_0 + \Delta\tau_1 + \Delta\tau_2 + \Delta\tau_3)$; the distance between two electrons is enough large and thus the Coulomb interactions between them are attractive. (e) $\mathbf{H} \neq 0$ $(\tau = \tau_0 + \Delta\tau_1 + \Delta\tau_2 + \Delta\tau_3 + \Delta\tau_4)$; the distance between two electrons is very small and thus the Coulomb interactions between them are repulsive.

conductivity can occur. Therefore, we can expect that the normal electrical conductivity can occur if electron−phonon coupling constants for the electronic states ($l_{\text{electronic state}}$) are not zero ($l_{\text{electronic state}} \neq 0$) (Figure 1b).

In the macroscopic materials such as graphite (Scheme 1c), even in a case where the valence band is completely occupied by electrons, the $l_{\text{electronic state}}$ values are not zero because the second-order perturbation effects are important (Figure 1c).

$$l_{\text{electronic state}} = l_{\text{neutral}} + l_{\text{second order}} = l_{\text{second order}} \neq 0 \quad (6)$$

Furthermore, in such a case, the total momentum states of electrons can be also easily changed continuously by applied electric fields, and thus electrical conductivity can occur. Actually, bulk-sized graphite exhibits semimetallic behavior.

Even if we divide bulk graphite into two pieces, such half-sized graphite materials would still exhibit semimetallic behavior (Figure 1c). However, if we repeatedly divide bulk graphite into two pieces, the energy difference between the occupied and unoccupied orbitals becomes larger with a decrease in material size. If we divide bulk graphite into two pieces repeatedly and the size of each divided graphite piece becomes very small such as that of benzene (Scheme 1b,c), electron configurations can be finally expressed by Figure 1a. In a case where the HOMO is completely occupied by electrons in such small molecules (for example, neutral benzene and [18]annulene (Scheme 1b)), the total momentum states of electrons cannot be easily changed continuously by applied electric field, and thus the normal electrical conductivity cannot occur. Furthermore, in this case, the $l_{\text{electronic state}}$ values ($l_{\text{electronic state}} = l_{\text{neutral}} = 0$) originating from the first-order perturbation effects are zero (eqs 2 and 3) (Figure 1a).

In summary, finite $l_{\text{electronic state}}$ values for electronic states are closely related to the electrical conductivity; the total momentum states of electronic states that have finite $l_{\text{electronic state}}$ values can be easily changed by the applied electric field. The condition under which normal electrical conductivity can occur is more easily realized with an increase in material (molecular) size because the second-order perturbation effects as well as the first-order perturbation effects become important. On the other hand, at the same time, large $l_{\text{electronic state}}$ values result in the large electrical resistivity.

## Intraatomic Diamagnetic Currents

Electronic and magnetic properties in the normal solids have been studied by many researchers for a long time. However, the mechanism of intraatomic diamagnetic current in the neutral He atoms has not been elucidated. In this section, we provide an explanation of the intraatomic diamagnetic currents in closed-shell electronic structures in the neutral He atoms.

**Atomic Orbitals in the Neutral He Atom.** Energy levels of the atomic orbitals in the neutral He atoms are shown in Figure 3. In the neutral He atoms, 1s atomic orbitals are the highest occupied atomic orbitals (HOAO), which are completely occupied by two electrons, and 2s atomic orbitals are the lowest unoccupied atomic orbitals (LUAO). The energy difference ($\Delta E^{\text{He,1s}}_{\text{HOAO-LUAO}}$) between the HOAO and LUAO is estimated to be 48.2 eV by using the hybrid Hartree−Fock (HF)/density-functional-theory (DFT) method of Becke[19] and Lee, Yang, and Parr[20] (B3LYP) and the 6-31G* basis set,[21] as in our previous studies.[12] The GAUSSIAN 03 program package[22] was used for our theoretical analyses.

**Intraatomic Current in the Neutral He Atom.** In this section, we emphasize the problems of the mechanism of the intraatomic diamagnetic currents in the neutral He atoms and show why we cannot understand the intraatomic diamagnetic currents in the neutral He atoms (Figure 1a) only in terms of the mechanism of electrical conductivity in normal metals in detail.[1,9−11]

The intraatomic diamagnetic current intensity ($\sigma_{\text{intraatomic}}$) is obtained from[18]

$$\sigma_{\text{intraatomic}} \propto \mathbf{H}\,\text{AC} \tag{7}$$

where $\mathbf{H}$ is the applied magnetic field (taken to be perpendicular to the plane on which intraatomic diamagnetic currents occur) and AC is given by

$$\text{AC} = J_{\text{AC}} S \tag{8}$$

where $S$ is the area on which 1s electrons move around a He atom, and $J_{\text{AC}}$ is the induced intraatomic diamagnetic current.

Let us next investigate the possible mechanism of the intraatomic diamagnetic current in the neutral He atoms. Intraatomic diamagnetic currents of 1s electrons in the neutral He atoms are shown in Figure 4. When the electric (or magnetic) field is not applied, each electron in the 1s orbital would go around the He atomic nucleus, $+\mathbf{k}$, clockwise, and $-\mathbf{k}$, counterclockwise. Because the sum of all $\mathbf{k}_{1s}$ values is equal to zero (Figure 1a), the total intraatomic diamagnetic electron mobility becomes zero ($\sigma_{\text{total,intraatomic He}} = 0$), as expected, when no electric (or magnetic) field is applied ($\mathbf{E} = 0$ and $\mathbf{H} = 0$), as shown in Figure 4a.

Even in an applied magnetic field ($\mathbf{H} \neq 0$) (Figure 4b−e), the Fermi surface could not move as a whole to the direction parallel to the electric field $\mathbf{E}$. This can be understood as follows. The total momentum states of electrons of He atoms cannot be easily changed by applied electric fields (Figure 1a) because the energy difference between the HOAO and LUAO is very large ($\Delta E^{\text{He,1s}}_{\text{HOAO-LUAO}} = 48.2$ eV) in the neutral He atom. Therefore, the intraatomic diamagnetic current in the neutral He atoms cannot be explained in terms of the forming of the normal metallic states with large material sizes. One of possible mechanisms of forming of nondissipative intraatomic diamagnetic current in the neutral He atoms with microscopic sizes is the Bose−Einstein condensation as a consequence of attractive electron−electron interactions. The problem is how electron−electron interactions become attractive in the neutral He atoms with microscopic size, in which momentum states of electrons in the 1s atomic orbital cannot be easily changed by applied fields such as electric or magnetic field available in the laboratory (Figure 1a).

**Interactions between Two Electronic States.** Here, to see the difference between the normal superconductivity with large sizes and intraatomic diamagnetic currents in He atoms with microscopic sizes, we discuss the normal superconductivity in solids as well as intraatomic diamagnetic currents in He atoms with microscopic sizes. The discussions on conventional superconductivity can be extracted from several articles, for example, such as ref 14e.

According to the BCS theory in the conventional superconductivity with macroscopic sizes, a two-particle scattering matrix element $\langle \mathbf{k}',-\mathbf{k}'|V_{\text{eff}}|\mathbf{k},-\mathbf{k}\rangle$, which denotes a two-particle scattering matrix element for particles on opposite sides of the Fermi surface, from a two-particle state $|\mathbf{k},-\mathbf{k}\rangle$ to a two-particle state $\langle \mathbf{k}',-\mathbf{k}'|$, can be defined as[14e]

$$a_{\mathbf{k}}[2\epsilon_{\mathbf{k}} - E] = -\sum_{\mathbf{k}'} a_{\mathbf{k}'}\langle \mathbf{k}',-\mathbf{k}'|V_{\text{eff}}|\mathbf{k},-\mathbf{k}\rangle \tag{9}$$

## Possible Mechanism of the Occurrence of Intraatomic Diamagnetic Current in the Neutral He Atoms

**Electron−Electron Interactions in Conventional Superconductivity with Macroscopic Size.** In the previous section, we consider a quite general case, and we now specialize to the case where this scattering matrix element is one of the somewhat peculiar nature described above, that is, attractive in a thin shell around the Fermi surface, and zero elsewhere.[14] Considering the fact that we are looking into a thin shell around the Fermi surface, and assuming that the density of state $N(\epsilon)$ varies slowly, we may simply replace it by its value on the Fermi surface, $N(\epsilon_F)$. Introducing the dimensionless electron−phonon coupling constant $\lambda \equiv VN(\epsilon_F)$, we obtain[14e]

$$1 = \lambda \int_{\epsilon_F}^{\epsilon_F+\omega_0} \frac{d\epsilon'}{2\epsilon' - E} = \lambda \ln\left\{\frac{2(\epsilon_F + \omega_0) - E}{2\epsilon_F - E}\right\} \tag{10}$$

Then the energy difference between the states of two interacting particles on the Fermi surface, and the exact energy eigenvalue $E$, i.e., $\Delta_{\text{BCS}} = 2\epsilon_F - E$, is introduced. In terms of this variable, eq 10 may be written[14e]

$$\Delta_{\text{BCS}} = \frac{2\omega_0}{e^{1/\lambda} - 1} \approx 2\omega_0 e^{-1/\lambda} \tag{11}$$

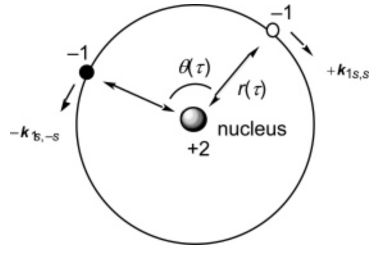

**Figure 5.** Two electrons in the 1s atomic orbital and a nucleus in the neutral He atom. Opened and closed circles represent electrons moving around the nucleus represented by large shaded circle, clockwise, and counterclockwise, respectively.

The superconducting transition temperature $T_{c,BCS}$ is defined by

$$T_{c,BCS} \propto \Delta(0)_{BCS} = 2\omega_0 e^{-1/\lambda} \tag{12}$$

where the last approximation follows if $\lambda \ll 1$ (if the effective electron−electron attraction is weak). Because of the exponential factor $\lambda$ in eq 12 and low Debye frequencies ($\omega_0 \sim 10^2$ K) in the conventional superconductors with macroscopic sizes, the $T_{c,BCS}$ values usually cannot become very large. For example, Nb has the highest $T_{c,BCS}$ (9.2 K) found in any element, and $Nb_3Ge$ has the $T_{c,BCS}$ (23.2 K) and $MgB_2$ has the highest $T_{c,BCS}$ (39 K) found in any binary alloy.[14] Superconductivity in alkali metal-intercalated graphite compounds, i.e., graphite intercalation compounds (GICs) (Scheme 1c), was reported in 1965.[23] The superconductivity in GICs have extensively been studied and new compounds have been synthesized since 1978.[24] Superconducting transition temperatures for GICs, however, are very low, and 5.5 K for $C_4K$ at highest.[25,26] The alkali metal-doped $A_3C_{60}$ complexes[27] were found to exhibit $T_{c,BCS}$ of more than 30 K[28] and 40 K under pressure.[29] It has been suggested that pure Raman-active modes are important in a BCS-type[13,14,30] strong coupling scenario in superconductivity in alkali metal-doped fullerenes.[30] The key to superconductivity at high temperatures (35 K) was found in 1986 with the discovery of a new class of superconductors based on copper oxide ceramics with layered crystal structures.[31] Still today, copper and oxygen are the key compounds to form superconductors and have the highest $T_c$ of 135 K.[14]

**Possible Formation of the Electron Pair in the Neutral He Atoms with Microscopic Sizes.** In the neutral He atoms with microscopic sizes, the above discussions cannot be made. That is, the electron−phonon interactions would not play an essential role in the forming of electron pairing. Thus, another mechanism should be investigated. In this paper, we consider the extra energy lowering of $V_{Coulomb}^{He,1s}$ originating from the attractive electron−electron interactions between two electrons with opposite spins occupying the 1s atomic orbital (i.e., $+\mathbf{k}_{1s,\uparrow}$ and $-\mathbf{k}_{1s,\downarrow}$). From this assumption, $V_{eff}$ in eq 13 can be expressed as

$$\langle \mathbf{k}',-\mathbf{k}'|V_{eff}|\mathbf{k},-\mathbf{k}\rangle = -V_{Coulomb}^{He,1s}\delta_{\mathbf{k},\mathbf{k}'} \tag{13}$$

Using this equation, eq 9 takes the form

$$\Delta_{\mathbf{k}} = 2\epsilon_{\mathbf{k}} - E = V_{Coulomb}^{He,1s}\delta_{\mathbf{k},\mathbf{k}'} \tag{14}$$

**Coulomb Interactions in the Neutral He Atoms.** Let us next look into the Coulomb interactions between electrons. Here, for simplicity, we consider that two electrons move around a He nucleus as shown in Figure 5. In this figure, $r(\tau)$ denotes the intraatomic distance between an electron occupying the 1s atomic orbital and a nucleus in the He atom at time $\tau$, and $\theta(\tau)$ denotes the 1s electron−nucleus−1s electron angles at time $\tau$. The most probable $r(\tau)$ value is 0.265 Å in the neutral He atoms.[32] Intraatomic diamagnetic currents of two electrons occupying the 1s orbital at time $\tau$ in the neutral He atom are shown in Figure 4. Let us investigate how the strengths of Coulomb interaction between two electrons occupying 1s atomic orbital in the same He atom changes by moving of these electrons in detail (Figure 4). These electrons rapidly move around a He nucleus and electron distributions on a He atom significantly change in a short time, as shown in Figure 4. Here, we consider the average Coulomb energy ($V_{Coulomb}^{He,1s} = \langle V_{Coulomb}^{He,1s}(\tau)\rangle_{av,\tau}$) observed for a long time. The direct Coulomb interactions ($V_{Coulomb}^{He,1s}(\tau)$) between two electrons at $\tau$ are

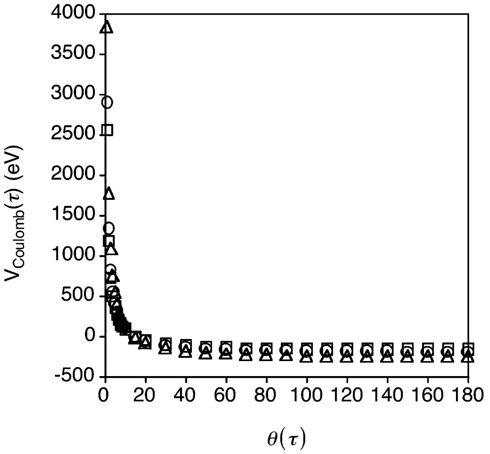

**Figure 6.** Coulomb interaction energy as a function of $r(\tau)$ and $\theta(\tau)$. The triangles, circles, and squares represent the Coulomb interaction energies estimated by considering the $r(\tau)$ values of 0.200, 0.265, and 0.300 Å, respectively. In this figure, Coulomb interaction energies for $\theta(\tau)$ values ranging between 1 and 180° are shown.

$$V_{Coulomb}^{He,1s}(\tau) = \frac{e^2}{4\pi\epsilon_0 r(\tau)}\left\{-4 + \frac{1}{2\sin(\theta(\tau)/2)}\right\} \tag{15}$$

Let us next look into the Coulomb interactions between two electrons occupying the 1s atomic orbital in the neutral He atom, to investigate whether the Coulomb interactions become attractive (Figure 4b,d). The estimated $V_{Coulomb}^{He,1s}(\tau)$ values as a function of $r(\tau)$ and $\theta(\tau)$ are shown in Figure 6. The triangles, circles, and squares represent the $V_{Coulomb}^{He,1s}(\tau)$ values estimated by considering the $r(\tau)$ values of 0.200, 0.265, and 0.300 Å, respectively. We can see from this figure that the $V_{Coulomb}^{He,1s}(\tau)$ values become negative when $\theta(\tau) > 15$. The $V_{Coulomb}^{He,1s}(\tau)$ values decrease with an increase in $\theta(\tau)$ value, and the $|V_{Coulomb}^{He,1s}(\tau)|$ values decrease with an increase in $r(\tau)$ value, as expected. Furthermore, we can see that the $V_{Coulomb}^{He,1s}(\tau)$ values are negative in most of the time and are about −180 eV, and the $V_{Coulomb}^{He,1s}(\tau)$ values can become very large positive values only for very short time.

To estimate the $\langle V_{Coulomb}^{He,1s}(\tau)\rangle_{av,\tau}$ ($=V_{Coulomb}^{He,1s}$) value, the total energy at 298 K is calculated in the neutral He atom by using the B3LYP/6-31G* level. The estimated energy is −113.1 eV in the neutral He atom. This means that $\langle V_{Coulomb}^{He,1s}(\tau)\rangle_{av,\tau} \approx -113.1$ eV. Therefore, most of the time, the interaction between two electrons occupying 1s atomic orbital is attractive. The $V_{Coulomb}^{He,1s}(\tau)$ value becomes −113.1 eV when $r(\tau) \approx 0.265$ Å and $\theta(\tau) \approx 14.4°$.

## Second-Order Perturbation Effects

At a much higher temperature than room temperature, an electron promotion from the HOAO to the LUAO can occur and thus the second-order perturbation effects become more important with an increase in temperature (Figure 3b). Therefore, the electron pairs are destroyed at higher temperatures. The critical temperature at which an electron pair in the ground state in each He atom is destroyed is defined as

$$T_{\mathrm{c,HOAO-LUAO}}^{\mathrm{He,1s}} \propto \Delta E_{\mathrm{HOAO-LUAO}}^{\mathrm{He,1s}} \tag{16}$$

The critical temperature $T_{\mathrm{c}}^{\mathrm{He,1s}}$ at which the intraatomic diamagnetic current disappears in each neutral He atom can be defined as

$$T_{\mathrm{c}}^{\mathrm{He,1s}} \propto \Delta(0)_{\mathrm{He,1s}} = \min(\Delta E_{\mathrm{HOAO-LUAO}}^{\mathrm{He,1s}}, V_{\mathrm{Coulomb}}^{\mathrm{He,1s}}) = \Delta E_{\mathrm{HOAO-LUAO}}^{\mathrm{He,1s}} \tag{17}$$

Let us next look into macroscopic materials. Because the energy gap ($\Delta E_{\mathrm{HOCO-LUCO}}$ value) between the HOCO and LUCO decreases with an increase in material size, the second-order perturbation effects become more important with an increase in material size. Therefore, the mechanism of intraatomic diamagnetic current suggested in this research would not be true for materials with large sizes, and the normal metallic state would appear in materials with large sizes. Therefore, if the material is made arbitrarily large such as in graphite (Scheme 1c), bulk superconductivity does not result because, as the system gets bigger, the different momentum states of the electrons approach each other in energy (Figure 1c). Transitions can then occur between states and the induced currents are dissipated. To get superconductivity in a macromolecule or in a bulk material, something of the nature of a coherence energy is required. In conventional superconductors such as GICs (Scheme 1c), this is provided by the phonon-induced electron−electron interaction.

The $T_{\mathrm{c}}^{\mathrm{He,1s}}$ values for the neutral He atoms with microscopic sizes are estimated to be much larger than the $T_{\mathrm{c,BCS}}$ values for the conventional superconductors with macroscopic sizes. This is because both the $\Delta_{\mathbf{k}}$ and $\Delta E_{\mathrm{HOAO-LUAO}}^{\mathrm{He,1s}}$ values for the neutral He atoms with microscopic sizes are larger than the $\Delta_{\mathrm{BCS}}$ and $\Delta E_{\mathrm{HOCO-LUCO}}$ values for the conventional superconductors with macroscopic sizes. The 1s and 2s atomic orbitals are well separated from each other in the neutral He atoms, and thus we consider the Coulomb interactions between two electrons occupying only the 1s atomic orbital to estimate the total Coulomb energies. Therefore, the energy lowering as a consequence of attractive electron−electron interactions is proportional to an energy gap that must be overcome so such an electron pair is destroyed ($T_{\mathrm{c,Coulomb}}^{\mathrm{He,1s}} \propto \Delta_{\mathbf{k}} \propto V_{\mathrm{Coulomb}}^{\mathrm{He,1s}}$) (eq 14). On the other hand, in the conventional superconductivity, the energy lowering factor as a consequence of the attractive electron−electron interactions $\lambda$ appears in the exponential factor in the equation for $T_{\mathrm{c,BCS}}$ ($T_{\mathrm{c,BCS}} \propto \Delta(0)_{\mathrm{BCS}} \propto \mathrm{e}^{-1/\lambda}$) (eq 12). Such an exponential factor appears because electronic states are very close to each other in conventional superconductors with macroscopic sizes, and we must consider energy-space or **k**-space integrals continuously in a thin shell around the Fermi surface (eq 10). Furthermore, the $\Delta E_{\mathrm{HOCO-LUCO}}$ value is usually very small in conventional superconductivity. In summary, the energy lowering factor in the exponential factor $\lambda$ in the equation for $T_{\mathrm{c,BCS}}$, the very small $\Delta E_{\mathrm{HOCO-LUCO}}$ values (originating from continuous energy levels of electronic states in the conventional superconductors with macroscopic sizes), the energy lowering factor (which is proportional to the $V_{\mathrm{Coulomb}}^{\mathrm{He,1s}}$ and $T_{\mathrm{c,Coulomb}}^{\mathrm{He,1s}}$), and the very large $T_{\mathrm{c,HOAO-LUAO}}^{\mathrm{He,1s}}$ value (originating from discrete energy levels of electronic states in the neutral He atoms with microscopic sizes) are the main reasons that the $\Delta E_{\mathrm{HOAO-LUAO}}^{\mathrm{He,1s}}$ and $\Delta_{\mathbf{k}}$ values (i.e., $T_{\mathrm{c}}^{\mathrm{He,1s}}$ values) for the neutral He atoms with microscopic sizes are estimated to be much larger than the $\Delta E_{\mathrm{HOCO-LUCO}}$ and $\Delta_{\mathrm{BCS}}$ values (i.e., $T_{\mathrm{c,BCS}}$ values) for the conventional superconductors with macroscopic sizes.

## Bulk Systems

Let us look into bulk systems. It should be noted that we can expect only intraatomic diamagnetic current in some of the neutral He atoms, and in the bulk system, the interatomic current cannot be expected to be observed because interatomic electron transfer cannot be expected in closed-shell electronic structures in the He atoms with microscopic sizes. However, it should be noted that in the conventional superconductivity with macroscopic sizes, the interatomic or intermolecular supercurrent occurs in bulk systems. Furthermore, it should be noted that in the high-temperature region but below the critical temperature $T_{\mathrm{c,BCS}}$, conventional superconductivity is always retained for the states in the bulk system, whereas the intraatomic diamagnetic current disappears and appears alternately for a long time and some of the neutral He atoms exhibit intraatomic diamagnetic current and other He atoms do not exhibit intraatomic diamagnetic current. If we look into a He atom for a long time in an applied magnetic field, the intraatomic diamagnetic current occurs at time $\tau_0 + \Delta\tau_1$ (Figure 4b), and then it disappears in the neutral He atom and the neutral He atom becomes an intraatomic insulator at time $\tau_0 + \Delta\tau_1 + \Delta\tau_2$ (Figure 4c). Then the intraatomic diamagnetic current occurs again in the neutral He atom at time $\tau_0 + \Delta\tau_1 + \Delta\tau_2 + \Delta\tau_3$ (Figure 4d) and disappears at time $\tau_0 + \Delta\tau_1 + \Delta\tau_2 + \Delta\tau_3 + \Delta\tau_4$ (Figure 4e). That is, intraatomic diamagnetic current states and insulating states appear alternately for a long time. However, in view of Figure 6, we can expect that the electron configurations formed by two electrons occupying the 1s atomic orbital are in the intraatomic diamagnetic current states (Figure 4b,d) most of the time. We can expect that, most of the time, the electron−electron interaction between two electrons occupying the 1s atomic orbital is attractive and the electronic states in the neutral He atom are in intraatomic diamagnetic current states (Figure 4b,d). This can be also rationalized from ab initio calculated results that the average Coulomb energy observed for a long time is negative ($\langle\langle V_{\mathrm{Coulomb}}^{\mathrm{He,1s}}(\tau)\rangle_{\mathrm{av},\tau} \approx -113.1$ eV) in the neutral He atom.

## Intraatomic Diamagnetic Nondissipative Current in the Neutral He Atom

By analogy with the conventional superconductivity in the BCS theory,[13,14] an electron pair for the neutral He atom at time $\tau$ can be expressed as

$$\Phi_{\mathrm{He,1s}}(\tau) = a(\tau)\phi_{\mathrm{He,1s}}(+\mathbf{k}_{1\mathrm{s},\uparrow}, -\mathbf{k}_{1\mathrm{s},\downarrow}) \tag{18}$$

When the attractive interaction between two electrons dominates over the repulsive interactions in the neutral He atom, the system would produce an electron pair. The ground-state wave function in the electron pairing states in the neutral He atom with microscopic sizes at time $\tau$ can be expressed as

$$\psi_{0\mathrm{He,1s}}(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_{n_{\mathrm{total}}},\tau) = \Phi_{\mathrm{He,1s}}(\mathbf{r}_1,\mathbf{r}_2,\tau)\ \Phi_{\mathrm{He,1s}}(\mathbf{r}_3,\mathbf{r}_4,\tau)\ ...\ \Phi_{\mathrm{He,1s}}(\mathbf{r}_{n_{\mathrm{s}}-1},\mathbf{r}_{n_{\mathrm{s}}},\tau) \tag{19}$$

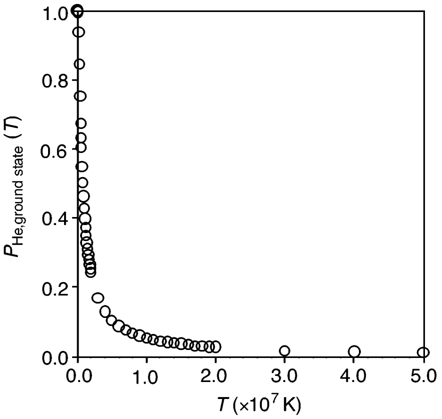

**Figure 7.** $P_{\mathrm{He,ground\ state}}(T)$ values as a function of temperature in the neutral He atoms.

where $n_s$ is the number of electrons forming electron pairs in the neutral He atomic bulk systems.

The intraatomic diamagnetic current state is in a constrained condition such that the momentum of the paired electrons cannot be altered at will. Indeed, the energy $2\Delta(0)_{\mathrm{He,1s}}$ is needed to destroy the intraatomic diamagnetic current state at 0 K. As a consequence, the scattering that changes the direction of the wave vector is prohibited for the paired electrons. Once a current is induced, each electron pair acquires the same velocity vector $\mathbf{k}_{\mathbf{H},\mathrm{induced}}/m_e$ in parallel to the applied field, according to eqs 7 and 8, where $m_e$ denotes the mass of an electron. Thus, the drift velocity of all electron pairs must be $\mathbf{k}_{\mathbf{H},\mathrm{induced}}/m_e$ and all the electron pairs acquire the same momentum and move in a direction parallel to the field. A current flowing without disturbing the ordered state is indeed a resistanceless conduction. Therefore, once a current is induced by applying the magnetic field to a He atom, it persists as long as the electron pairs remain stable in the neutral He atom, according to eqs 7 and 8.

## Statistical Discussions in the Bulk Systems

In the previous sections, we looked into only one He atom by assuming that the electronic structure in each He atom behaves independently. On the other hand, when we observe electronic structures in many He atoms in bulk systems, we must consider these electronic structures from a statistical point of view. In the neutral He atom with microscopic size, a transition from the intraatomic diamagnetic current state to an insulating state as a consequence of an electron promotion from the HOAO to LUAO would occur at $T_c^{\mathrm{He,1s}}$ ($T_{\mathrm{c,HOAO-LUAO}}^{\mathrm{He,1s}}$) before an electron pair in the ground state in each atom is destroyed at $T_{\mathrm{c,Coulomb}}^{\mathrm{He,1s}}$. The number of He atoms in which both the HOAO and LUAO are partially occupied by an electron increases with an increase in temperature. The ratio of the number of He atoms with ground states ($n_{\mathrm{ground\ state}}(T)$) to that of all He atoms ($n_{\mathrm{total}}$) at $T$ K is defined as

$$P_{\mathrm{He,ground\ state}}(T) = \frac{n_{\mathrm{ground\ state}}(T)}{n_{\mathrm{total}}} = 1 - \exp(-\Delta E_{\mathrm{HOAO-LUAO}}^{\mathrm{He,1s}}/k_B T) \quad (20)$$

$P_{\mathrm{He,ground\ state}}(T)$ values as a function of temperature $T$ (K) are shown in Figure 7. The $P_{\mathrm{He,ground\ state}}(T)$ value significantly decreases in the region between $1 \times 10^5$ and $2 \times 10^6$ K. $P_{\mathrm{He,ground\ state}}(T)$ values in this region are listed in Table 1. We can see from Figure 7 that at 298 K, electronic states in most of the He atoms are in the ground state. Therefore, the intraatomic diamagnetic currents exist in most of the He atoms at 298 K. However, it should be noted that dependence of electronic properties on temperature in the diamagnetic currents in the neutral He atoms with microscopic sizes is essentially different from that in the conventional superconductivity with macroscopic sizes, as follows. In the conventional superconductivity with macroscopic sizes, even in the high-temperature region but below the critical temperature $T_{\mathrm{c,BCS}}$, conventional superconductivity is always retained for the states in the bulk system, and above the $T_{\mathrm{c,BCS}}$, the supercurrent in the conventional superconductor with macroscopic sizes completely disappears. On the other hand, in the neutral He atoms with microscopic sizes, in principle, even below the temperature $T_c^{\mathrm{He,1s}}$, intraatomic diamagnetic currents in some of the He atoms disappear, even though intraatomic diamagnetic currents would be observed in almost all He atoms most of the time at 298 K. Furthermore, even above the critical temperature $T_c^{\mathrm{He,1s}}$, there are some He atoms where intraatomic diamagnetic currents can exist. That is, the critical temperature $T_{\mathrm{c,BCS}}$ can be predicted somewhat clearly but the critical temperatures $T_c^{\mathrm{He,1s}}$ in one He atom cannot be predicted precisely and we can predict $T_c^{\mathrm{He,1s}}$ values only statistically in the bulk system. However, in this research, we can at least conclude that we would observe intraatomic diamagnetic currents in almost all He atoms at 298 K as a consequence of the attractive Coulomb interactions between two electrons occupying the 1s atomic orbital in each neutral He atom.

**TABLE 1: $P_{\mathrm{He,ground\ state}}(T)$ Values as a Function of $T$ Ranging between 1.0 × $10^5$ and 20.0 × $10^5$ K**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $T$ ($10^5$ K) | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 | 7.0 |
| $P_{\mathrm{He,ground\ state}}(T)$ | 0.996 | 0.939 | 0.845 | 0.753 | 0.673 | 0.606 | 0.550 |
| $T$ ($10^5$ K) | 8.0 | 9.0 | 10.0 | 11.0 | 12.0 | 13.0 | 14.0 |
| $P_{\mathrm{He,ground\ state}}(T)$ | 0.503 | 0.463 | 0.428 | 0.398 | 0.372 | 0.349 | 0.329 |
| $T$ ($10^5$ K) | 15.0 | 16.0 | 17.0 | 18.0 | 19.0 | 20.0 | |
| $P_{\mathrm{He,ground\ state}}(T)$ | 0.311 | 0.295 | 0.280 | 0.267 | 0.255 | 0.244 | |

Finally, let us briefly discuss the potential application of diamagnetic currents to electronics. As described in the previous section, we can only expect the intraatomic diamagnetic current in some of the neutral He atoms, and in the bulk system, the interatomic current cannot be expected because interatomic electron transfer cannot be expected in closed-shell electronic structures in the He atoms with microscopic sizes (Scheme 1a). Similar discussions can be made in microscopic molecular systems such as benzene and [18]annulene (Scheme 1b), as discussed in the previous research.[12] As discussed in the previous section, because the $\Delta E_{\mathrm{HOCO-LUCO}}$ value decreases with an increase in material size, the second-order perturbation effects become more important with an increase in material size (Figure 1c). Therefore, the mechanism of intraatomic diamagnetic current suggested in this research would not be true for materials with large sizes, and the normal metallic state would appear in materials with large sizes. However, if a bulk system has a closed-shell electronic structure and large energy difference between the occupied and unoccupied orbitals, as shown in Figure 1a, such a bulk system has the possibility of exhibiting diamagnetic currents originating from the attractive Coulomb interactions between two electrons with opposite spins occupying the same orbitals (Figure 1a), from analogy with the nondissipative diamagnetic currents in microscopic atomic and molecular systems with closed-shell electronic structures. For example, pure diamonds have closed-shell electronic structures and large valence and conduction band gaps. Actually, the band gaps between the valence and conduction bands in pure diamonds are very large (5.47 eV).[33] Therefore, according to eq 20, the probability of the disappearance of the nondissipative diamagnetic current states is estimated to be very low ($\sim 10^{-93}$) at 298 K. In this sense, we can consider the bulk diamond system as a macroscopic molecule with large HOMO−LUMO gap. Furthermore, considering that the energy levels of occupied orbitals in pure diamonds are always negative, we expect that interactions between two electrons with opposite spins occupying the same orbitals can become attractive in pure diamonds, as discussed in He atoms and benzene and [18]-annulene molecules. On the other hand, in diamonds with macroscopic sizes, there is a very high possibility that some impurities or dopants exist. Even a very small ratio of impurities or dopants would destroy possible nondissipative diamagnetic current states in the diamonds with macroscopic sizes. The technology that enables us to produce very pure diamonds in which no impurities exist is awaited. It would be interesting to investigate the possibilities of the occurrence of nondissipative diamagnetic currents in bulk systems with closed-shell electronic structures and large energy differences between occupied and unoccupied orbitals such as pure diamonds as well as in microscopic atomic and molecular systems.

## Concluding Remarks

We investigated the mechanism of the occurrence of intraatomic diamagnetic currents in neutral He atoms with microscopic sizes. We found that most of the electrons can form electron pairs originating from attractive Coulomb interactions between two electrons with opposite spins occupying the 1s atomic orbital in the neutral He atom at 298 K. We suggested that intraatomic diamagnetic currents in the neutral He atoms with microscopic sizes can be explained by such electron pairing.

The $T_c^{\mathrm{He,1s}}$ value at which intraatomic diamagnetic currents can disappear in each He atom is estimated. The $T_c^{\mathrm{He,1s}}$ values for the neutral He atoms with microscopic sizes are estimated to be much larger than the $T_{c,\mathrm{BCS}}$ values for the conventional superconductors with macroscopic sizes. This is because both the $\Delta_{\mathbf{k}}$ and $\Delta E_{\mathrm{HOAO-LUAO}}^{\mathrm{He,1s}}$ values for the neutral He atoms with microscopic sizes are larger than the $\Delta_{\mathrm{BCS}}$ and $\Delta E_{\mathrm{HOCO-LUCO}}$ values for the conventional superconductors with macroscopic sizes. The energy lowering factor in the exponential factor $\lambda$ in the equation for $T_{c,\mathrm{BCS}}$, the very small $\Delta E_{\mathrm{HOCO-LUCO}}$ values (originating from continuous energy levels of electronic states in the conventional superconductors with macroscopic sizes), the energy lowering factor that is proportional to the $V_{\mathrm{Coulomb}}^{\mathrm{He,1s}}$ and $T_{c,\mathrm{Coulomb}}^{\mathrm{He,1s}}$, and the very large $T_{c,\mathrm{HOAO-LUAO}}^{\mathrm{He,1s}}$ value (originating from discrete energy levels of electronic states in the neutral He atoms with microscopic sizes) are the main reasons that the $\Delta E_{\mathrm{HOAO-LUAO}}^{\mathrm{He,1s}}$ and $\Delta_{\mathbf{k}}$ values (i.e., $T_c^{\mathrm{He,1s}}$ values) for the neutral He atoms with microscopic sizes are estimated to be much larger than the $\Delta E_{\mathrm{HOCO-LUCO}}$ and $\Delta_{\mathrm{BCS}}$ values (i.e., $T_{c,\mathrm{BCS}}$ values) for conventional superconductors with macroscopic sizes.

We can expect only intraatomic diamagnetic current in some of He atoms, and in the bulk system, the interatomic current cannot be expected to be observed because interatomic electron transfer cannot be expected in the neutral He atomic bulk systems. On the other hand, in the conventional superconductivity with macroscopic sizes, the interatomic or intermolecular superconductivity occurs in bulk systems. Furthermore, if we look into a He atom for a long time in an applied magnetic field, intraatomic diamagnetic current states and insulating states appear alternately. However, most of the time, we can expect that the electron configurations formed by two electrons with opposite spins occupying the 1s atomic orbital are in the intraatomic diamagnetic current state.

In general, because the HOCO−LUCO gap decreases with an increase in material size, the second-order perturbation effect becomes more important with an increase in material size. Therefore, the mechanism of the occurrence of intraatomic diamagnetic current in the neutral He atoms suggested in this research would not usually be true for materials with large sizes, and the normal metallic state would appear in macroscopic materials. Therefore, if the material system is made arbitrarily large, such as in graphite, bulk superconductivity does not result because, as the system gets bigger, the different momentum states of the electrons approach each other in energy. A transition can then occur between states, and the induced currents are dissipated. To get superconductivity in macroscopic materials, something of the nature of a coherence energy is required. In conventional superconductors such as GICs, this is provided by the phonon-induced electron−electron interaction.

We discussed the ratio of the number of He atoms with ground states to that of He atoms with excited states at various temperatures. We found that the dependence of electronic properties on temperature in the diamagnetic currents in the neutral He atoms with microscopic sizes is essentially different from that in conventional superconductivity with macroscopic sizes. In the conventional superconductivity with macroscopic sizes, even in the high-temperature region but below the critical temperature $T_{c,\mathrm{BCS}}$, conventional superconductivity is always retained for the states in the bulk system, and above the $T_{c,\mathrm{BCS}}$, the supercurrent in the conventional superconductor with macroscopic sizes completely disappears. On the other hand, in the neutral He atoms with microscopic sizes, in principle, even below the temperature $T_c^{\mathrm{He,1s}}$, intraatomic diamagnetic currents in some of the He atoms disappear, even though the intraatomic diamagnetic currents would be observed in almost all He atoms most of the time at 298 K. Furthermore, even above the critical temperature $T_c^{\mathrm{He,1s}}$, there are some He atoms where the intraatomic diamagnetic currents can exist. That is, the critical temperature $T_{c,\mathrm{BCS}}$ can be predicted somewhat clearly but the critical temperature $T_c^{\mathrm{He,1s}}$ in one He atom cannot be predicted precisely and we can predict $T_c^{\mathrm{He,1s}}$ values only statistically in the bulk system. However, we can at least conclude in this study that we would observe intraatomic diamagnetic currents in almost all He atoms at 298 K as a consequence of the attractive Coulomb interactions between two electrons occupying the 1s atomic orbital in each neutral He atom.

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