Novel Electron Correlation in the Scattering Continuum for a Stability Analysis of the Electron Pair in the "Atomic" Level#

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Wannier phenomenon is examined for a stability analysis of a time-reversal electron pair scattering. Imagine a pair of electrons interacting one another. It is found that the nature of the interelectron interaction is to stabilize the time-reversal scattering state. This nature survives even under the influence of a scattering center. To conclude, we shall prove the following results: 1) inside the reaction zone of the scattering center, one of the electrons is trapped, pressing the other electron to the barrier of the reaction zone, or letting the other electron go away over the barrier of the reaction zone, namely, a time-reversal scattering state of the electron pair is unstable, while 2) outside the reaction zone, if the critical radius r_c is reached, then the time-reversal scattering state of the electron pair is stabilized. The critical radius r_c has an intrinsic importance as a measure of the coherence length ξ of the Cooper pair that exhibits the time-reversal symmetry.

Recent discovery of superconductivity in doped fullerenes K_3C_{60} or Rb_3C_{60} has renewed our interest on the strange electronic structure associated with the phenomenon of zero resistance.[1—3] Essential to this phenomenon is the special stability of the two-electron scattering state, the so-called Cooper pair.[4] The Cooper pair is the pair of electrons which has mutually opposite spin and opposite linear momentum. According to the BCS theory of superconductivity,[5] electrons are scattering one another under the influence of phonons. Although electrons have the same charge and repel one another, the scattering by phonons let the electrons be paired. The strange electronic structure of the superconducting state is believed to be brought about by a phase transition in the system of such electron pairs.[5] In this connection, the density functional theory[6] of the superconducting phase transition is presented.[7]

In the search for the other possible microscopic mechanism of the attractive Cooper pairing force, one important observation is that the Cooper pair is a special case of the time-reversal pair.[8,9] This observation has enlarged our scope to the quest of the pairing force even in the large but finite system where the translational symmetry is absent.[10]

Our interest in this paper is not in the condensed-matter aspects of the time-reversal electron pairs but rather in the atomic-like aspects of the time-reversal electron pair itself. We consider a two-electron scattering at a single scattering center. A normal situation of the model may be that one electron is bound at the scattering center and the extra electron comes in and kicks out the electron formerly bound. The scattering state of the electron pair is then analyzed. This kind of model has been studied in a different context by Wannier,[11] whose method we shall apply to our present problem. Remarkably, we shall disclose disarmingly simple nature of the interelctron interaction which intrinsically guarantees the stability of the time-reversal pair of electrons, the Cooper pair as the special case. This nature survives even under the influence of the scattering center. Special interest is laid on the Cooper pairing mechanism in the novel doped fullerenes in comparison with the orthodox metallic superconductors.

1. Characteristics of the Electron-Pair Potential

Imagine a pair of electrons e_1, e_2 that are interacting one another through Coulombic potential $1/r_{12}$ (atomic units is used throughout in this paper unless otherwise stated) under the influence of an isotropic scattering center with charge Z and polarizability α as shown in Fig. 1.

The electrostatic potential V of the electron pair is then given as

$$V = 1/r_{12} - Z(1/r_1 + 1/r_2) - \alpha(1/2r_1^4 + 1/2r_2^4), \quad (1a)$$

with

$$r_{12} = (r_1^2 + r_2^2 - 2r_1r_2 \cos\theta)^{1/2}, \quad (1b)$$

where θ is the angle between the radial vectors $\boldsymbol{r}_1$, $\boldsymbol{r}_2$ of the electrons e_1, e_2. The "distance" of the electron pair as a whole from the scattering center may be measured

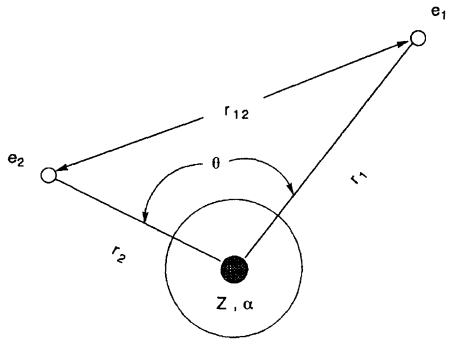

Fig. 1. A pair of electrons e_1, e_2 situated around the scattering center with charge Z and polarizability α. The θ is the angle between the radial vectors $\boldsymbol{r}_1$, $\boldsymbol{r}_2$ of the electrons e_1, e_2.

#In memory of the late Professor Hiroshi Kato.

by

$$r = (r_1^2 + r_2^2)^{1/2}. \tag{2}$$

Using this, we perform the variable transformation

$$r_1 = r \cos(\chi/2), \tag{3a}$$

$$r_2 = r \sin(\chi/2), \tag{3b}$$

with

$$0 < \chi < \pi. \tag{3c}$$

Then the interelectron repulsive potential term $1/r_{12}$ in V reduces to

$$1/r_{12} = 1/r(1 - \sin\chi \cos\theta)^{1/2}. \tag{4}$$

For r fixed, this term is demonstrated in Fig. 2 as a function of χ and θ.

It is easily found that the configuration P defined as

$$\mathrm{P} : \{\chi = \pi/2\ ,\ \theta = \pi\} \tag{5}$$

corresponds to the minimum of the potential $1/r_{12}$. Note that this configuration P exactly dictates the time-reversal configuration for the electron pair with respect to the scattering center: the radial vectors point to mutually opposite direction with the same distance, $r_1 = r_2$, from the scattering center. This disarmingly simple nature of the interelectron interaction has not been found in the literature. After the inclusion of the other terms of interaction with the scattering center, Eq. 1a reduces to

$$\begin{aligned} V = {} & 1/r(1 - \sin\chi \cos\theta)^{1/2} \\ & -Z(1/r \cos(\chi/2) + 1/r \sin(\chi/2)) \\ & -\alpha(1/2r^4 \cos^4(\chi/2) + 1/2r^4 \sin^4(\chi/2)). \end{aligned} \tag{6}$$

where the extremum character at the configuration P survives:

$$\partial V/\partial\theta = \partial V/\partial\chi = 0 \ \text{ at } \ \mathrm{P}. \tag{7}$$

At this configuration P, the potential V is plotted as a function of r in Fig. 3.

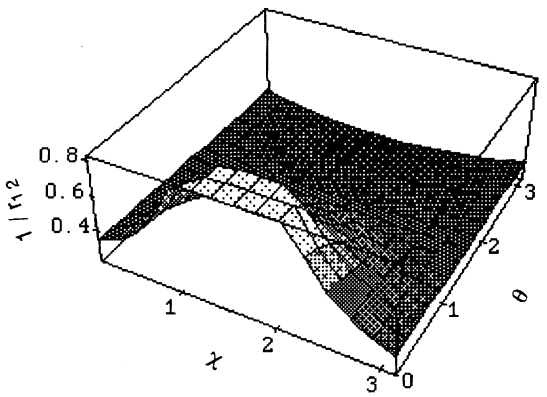

Fig. 2. Repulsive potential term $1/r_{12}$ as a function of χ and θ at r=3.

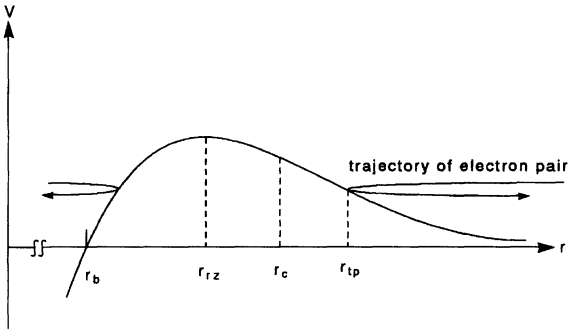

Fig. 3. Potential V as a function of r at the configuration P.

Then the reaction zone is separated from the scattering zone by the radius $r = r_{\mathrm{rz}}$ where the potential V takes the maximum value:

$$\partial V/\partial r = 0 \ \text{ at } \ r = r_{\mathrm{rz}}. \tag{8}$$

The r_{rz} is the characteristic radius that defines the reaction zone:

$$r_{\mathrm{rz}} = (4\sqrt{2}\alpha/(Z_{rz} - Z))^{1/3}, \tag{9a}$$

with

$$Z_{\mathrm{rz}} = 1/4. \tag{9b}$$

The Z_{rz} is the charge characteristic of the reaction zone.

Inside the reaction zone, the force acts to bind the electron pair at the scattering center. This means that the attractive potential term in V overwhelms inside the reaction zone. We further observe the characteristic radius r_{b} of electron-pair binding inside the reaction zone, within which the energy can take the negative value and the electron pair can be tightly bound:

$$V < 0 \ \text{ if } \ r < r_{\mathrm{b}}. \tag{10}$$

The two characteristic radii have the relationship:

$$r_{\mathrm{rz}} = 4^{1/3} r_{\mathrm{b}}. \tag{11}$$

It should be noted that if Z exceeds Z_{rz}, we have infinite value of r_{rz} and r_{b}:

$$r_{\mathrm{rz}} = \infty, \ \ r_{\mathrm{b}} = \infty, \ \ ; \ \text{ if } \ Z > Z_{\mathrm{rz}}. \tag{12}$$

This means that the interelectron repulsive term is completely smeared out by the attractive term.

Outside the reaction zone, the force acts to repel the electron pair from the scattering center, letting the electron pair escape in the scattering zone. Whether this extremum configuration P corresponds to the stable equilibrium configuration or the unstable equilibrium configuration should be judged by the eigenvalues of the Hessian of V. We then obtain the Hessian matrix elements as follows:

$$\begin{aligned} & \partial^2 V/\partial\theta^2 = (1/4\sqrt{2})(1/r) \\ & \partial^2 V/\partial\chi^2 = (3/\sqrt{2})(1/r^4)((Z_c - Z)r^3 - 8\sqrt{2}\alpha) \ ; \ \text{at P}, \\ & \partial^2 V/\partial\theta\partial\chi = 0 \end{aligned} \tag{13a}$$

with

$$Z_c = 1/12. \tag{13b}$$

The Z_c is the critical charge characteristic of the curvature of V. It is found that the configuration P is stable in the direction of θ, $\partial^2 V/\partial\theta^2 > 0$, and the situation is schematically shown in Fig. 4(a).

This is simply because of the repulsive term $1/r_{12}$: the electrons repel one another and the configuration $\theta=\pi$ should be most probable. On the other hand, it is conditionally stable along the direction of χ, as schematically shown in Fig. 4(b):

$$\begin{aligned} &\partial^2 V/\partial\chi^2 < 0 \ ; \ r < r_c \\ &\qquad\qquad\qquad\qquad ; \ \text{at P}, \\ &\partial^2 V/\partial\chi^2 > 0 \ ; \ r > r_c \end{aligned} \tag{14a}$$

where

$$r_c = (8\sqrt{2}\alpha/(Z_c - Z))^{1/3}. \tag{14b}$$

The r_c is the critical radius associated with Z_c. Inside the critical radius, $r<r_c$, the ridge appears in the potential V. Outside the critical radius, $r>r_c$, the ridge disappears in the potential V; instead, we observe valley in V. If the electron pair is situated outside the critical radius, then we have the stable trajectory by which the electron pair can escape away from the scattering center in a time-reversal manner.

Note that r_c is larger than r_{rz} because $Z_{rz} > Z_c$:

$$r_c = c r_{rz} \ ; \ c = (2(Z_{rz} - Z)/(Z_c - Z))^{1/3} > 1. \tag{15}$$

This shows that even if r exceeds r_{rz}, the two-electron scattering state is unstable if created inside the critical radius, because the Hessian has negative eigenvalue along the direction of χ. This situation is schematically shown in Fig. 5.

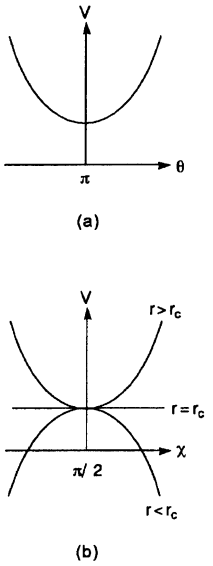

Fig. 4. Potential V: (a) along the direction θ, and (b) along the direction χ.

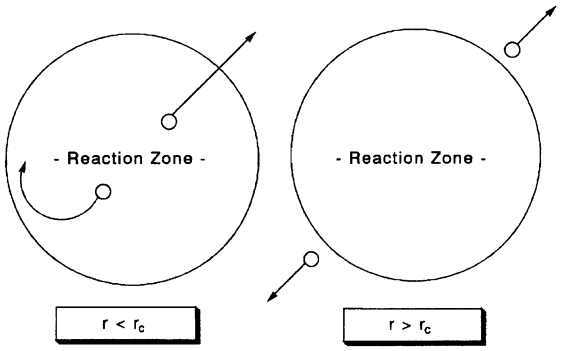

Fig. 5. Stability of the time-reversal electron pair.

Moreover, if Z exceeds Z_c but not Z_{rz}, then we obtain finite r_{rz} but not r_c any more:

$$r_c = \infty \ ; \ \text{if} \ \ Z_{rz} > Z > Z_c. \tag{16}$$

This shows that the repulsive term is not completely smeared out, but the attractive term is so strong that one electron will collapse to the scattering center, letting the other electron freely go away. In other words, if Z is in between Z_c and Z_{rz}, then we have no "outside" of the critical radius. Everywhere around the scattering center is classified as the "inside" of the critical radius, and hence the time-reversal scattering state becomes unstable.

2. Wannier Analysis of the Cooper Pair in C_{60}^{2-}+2e System

2.1 Characteristics of the Potential V. Using $Z=-2$ and $\alpha=10$ Å^3 (assumed) for the scattering center C_{60}^{2-}, the V of the electrons e_1, e_2 is demonstrated in Fig. 6a for $r=3.0$ fixed within r_c. As shown in Fig. 6a, the $\chi=\pi/2$ corresponds to the maximum of V. The unsymmetric character of r_1 and r_2 is evident because of the sharp valley towards $\chi=0$ or π. For $r=30.0$ that is sufficiently larger than r_c, we recover the situation that $\chi=\pi/2$ becomes minimum of the potential V, which is shown in Fig. 6b.

2.2 Stability of the Trajectory. The trajectory calculation has been performed. We assume, after Wannier,[11] spin-singlet s-wave scattering state for the electron pair. The Hamiltonian is then given as

$$\begin{aligned} H &= (1/2)(p_1^2 + p_2^2) + (1/2)(1/r_1^2 + 1/r_2^2)p_\theta^2 + V, \\ &= (1/2)[(p_r^2 + (4/r^2)p_\chi^2 + (4/r^2 \ \sin^2 \ \chi)p_\theta^2] + V, \end{aligned} \tag{17}$$

with the obvious notation of the momentums. The starting point of the calculation is the outer turning point, r_{tp}, located outside the reaction zone as shown in Fig. 3: We put r_{tp} larger than r_c. The other variables are randomly chosen: Along one of the trajectories, for example, the r, p_r are shown in Fig. 7 as a function of time together with the locus in the phase space (r, p_r). Outgoing wave for the electron pair is observed. For this trajectory, the χ, p_χ, and the locus in the phase

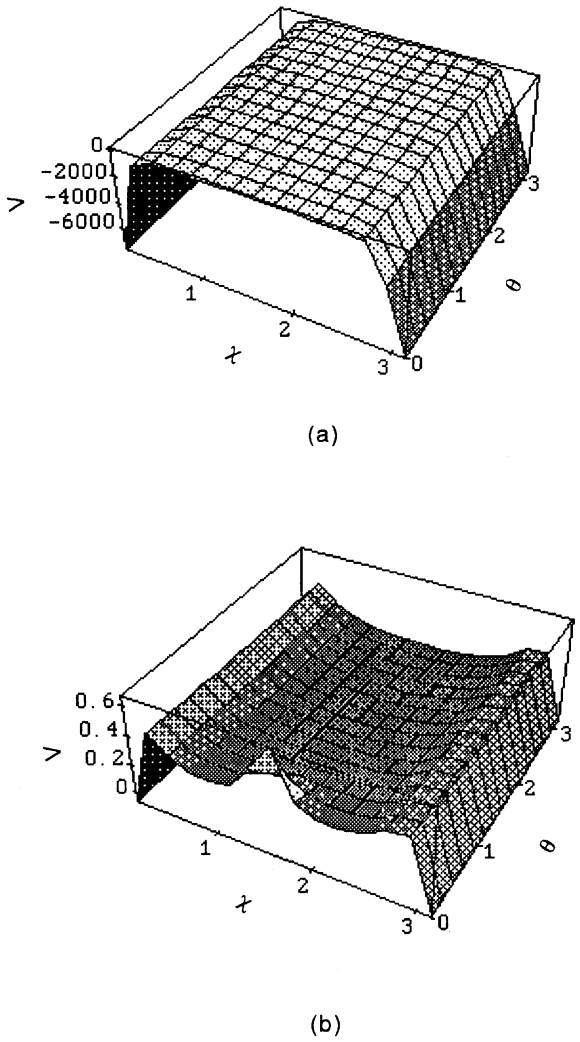

Fig. 6. Potential V at (a) $r=3.0$ within r_c, and (b) $r=30.0$ outside r_c.

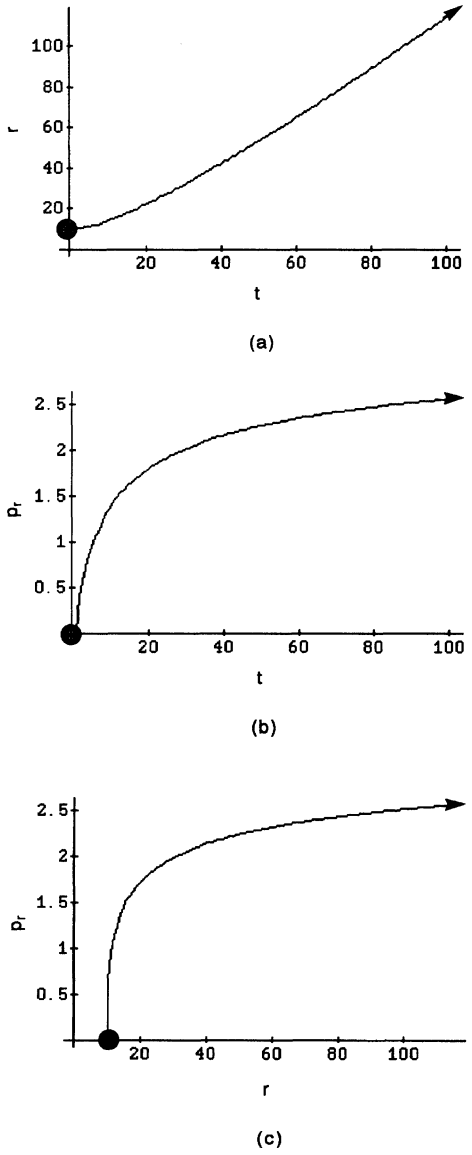

Fig. 7. Dynamic variables as a function of time: (a) r, (b) p_r, and (c) p_r vs. r.

space (χ, p_χ) are shown in Fig. 8. It is clearly demonstrated that the time-reversal trajectory is stabilized as time passes by.

3. Discussion

Our theory of the attractive force is not a "local" one, but a "dynamical" one as postulated in the BCS theory.[5] Indeed, our stabilization mechanism works whenever two electrons meet: There is no need to assign any specific local region of electron pair formation. The explicit treatment of the electron–electron scattering event shows that we are in a position over and above the simple Fermi liquid treatment. Here, it should be noted that if the interelectron interaction is attractive (again, no need to ask how it occurs), then superconductivity is brought about as proved by the BCS theory.[5]

The stability mechanism works even under the presence of the scattering center of the crystal lattice that exhibits the unique translational symmetry. The presence of the scattering center introduces the unstable region within which the time-reversal scattering state of the electron pair becomes unstable. The critical radius r_c is then a measure of the avoided region for the coherence of the electron pair. The wave function of the electron pair (the same function for all pairs in the BCS ground state[5]) should of course be a superposition of elementary geminal functions that are translational invariant. It is a matter of exercise to obtain a localized electron-pair function by unitary transformation of the translational invariant geminals; like a construction of the localized Wannier function by unitary transformation of the translational invariant Bloch functions in case of one-electron functions. The Bloch function and the Wannier function are obtained here for "electron-pair" functions in analogy with the one-electron functions. The local "Wannier function" of electron pair represents the time-reversal electron-pair scattering at

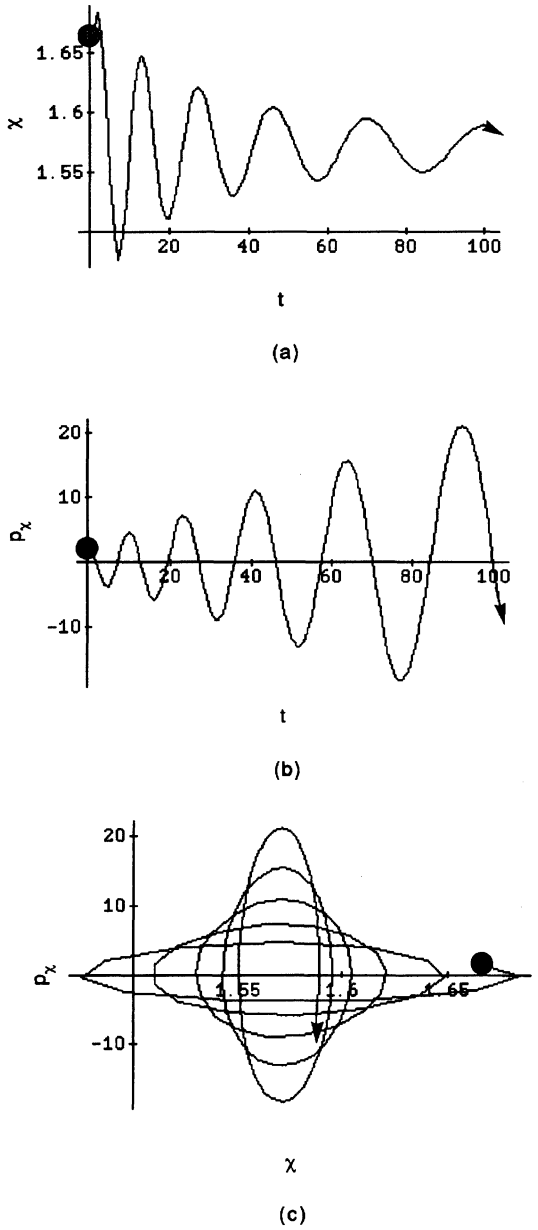

Fig. 8. Dynamic variables as a function of time: (a) χ, (b) p_χ, and (c) p_χ vs. χ.

each lattice point in the fundamental cell.

In the actual situation such as in the C_{60} superconductors, the crystal lattice points should act as the possible obstruction points to inhibit the electron pair formation. So that we shall examine how stable the electron pair is under the influence of the scattering center such as the C_{60} ball.

In the conventional low-temperature metallic superconductors, the quiescent Fermi sea should be situated in such a way that the charge neutrality is satisfied. This means that Z is equal to 2 if two electrons were initially bound at the scattering center or 1 if one extra electron attacks the electron initially bound at the scattering center. The Z in either case clearly exceeds Z_c and there is no room for the stable trajectory of the time-reversal electron pair. In the actual situation the nascent Coulombic potential should be screened. It follows that the effective Z should diminish as the electron pair escapes away from the scattering center. This leads to a large but finite r_c if the effective Z becomes smaller than Z_c: The electrons as a pair should be stabilized in a time-reversal manner at this large distance from the scattering center. Now that the electron pair is situated far away from the scattering center, it should be very difficult to neglect the influence of the other electrons which act to screen the nascent Coulombic potential, whose effect is opposite to the shielding effect of Z and make the electron pair unstable. The disturbance of the other electrons as well as phonons may destroy the time-reversal pair.

The discussion above strongly supports the observation that, in the orthodox low-temperature metallic superconductors, the coherence length ξ of the Cooper pair is very large, and it is the very low temperature which guarantees to minimize the disturbance that may destroy the time-reversality.

In the case of doped fullerenes A_3C_{60} (A=K or Rb), the alkali metals almost completely donate the outermost electrons to the C_{60} ball and formally constitute ionic molecular crystals $(A^+)_3C_{60}^{3-}$. We have found that C_{60} has large electron affinity up to the formation of C_{60}^{2-}.[12,13] The third electron is hardly bound.[14] The electronic ground state of C_{60}^{2-} is triplet as in agreement with the experimental fact,[15] and even the singlet state of C_{60}^{2-} is stable.[12—14] Up to the first order of the Jahn–Teller effect, the doublet C_{60}^{-} and the triplet C_{60}^{2-} does not show the Jahn–Teller instability of the nuclear framework in a fixed geometry, but the singlet C_{60}^{2-} shows it.[16] Even after the Jahn–Teller deformation occurred, the vibronic interaction in the singlet C_{60}^{2-} produces large vibronic attractive force with respect to the time-reversal electronic scattering process of the two electrons bound on the C_{60} ball.[12—14,16]

Thus the two electrons are bound on the C_{60} ball in a dual sense: 1) the large electron affinity of the C_{60} ball, and moreover, 2) the large vibronic attraction that stabilizes the time-reversal electron pair. These two electrons may then be situated within the reaction zone. On the other hand, the third electron, which is stoichiometrically belonging to the C_{60} ball together with the primary two electrons, may be situated outside the reaction zone. Consequently, it is most probable that the third electron is the outermost electron that is easily freed by the C_{60} ball. If the third electron is freed, then we may encounter the case of the free-electron-like behavior, which is observed by ESR measurement of the C_{60}^{3-},[15] and the resultant electron-pair stabilization in a time-reversal scattering state:

$$C_{60}^{3-} \rightarrow C_{60}^{2-} + e_1,$$
$$C_{60}^{3-} \rightarrow C_{60}^{2-} + e_2,$$

$$e_1 + e_2 \rightarrow (e_1, e_2) \quad \text{time} - \text{reversal electron pair}$$

The electron pair scattering state in the outgoing wave may be time-reversed to the incoming wave as shown in Fig. 9. This shows that if two electrons come close to the scattering center, then the time-reversal scattering is most probable.

The stability of such time-reversal scattering state is guaranteed by the mechanism proved in the preceding sections. The short r_c guarantees as minimum a disturbance, which may hence guarantee rather high T_c. Indeed, if we use the same α for C_{60}, C_{60}^{-}, and C_{60}^{2-}, then we obtain the critical radius r_c of these species as 11.0, 4.71, and 3.78 Å, respectively. These are all comparable with and larger than 3.59 Å that is the radius of C_{60} ball. The r_{rz} of these species in turn are 6.05, 3.56, and 2.92 Å. These value are compatible with the observation that C_{60}^{2-} does exists and is more stable than C_{60}^{3-}. The short coherence length observed in the novel high-T_c superconductors A_3C_{60} may correspond to the r_c for C_{60}^{2-}.

In this context, we may find an intrinsic measure of the coherence length ξ in the condensed phase level by calculating the critical radius r_c in the atomistic component level. This measure is excellent if the scattering center is rather localized as in the case of A_3C_{60}. In the actual situation, for example, the overlap of the time-reversal electron pair should play an important role for the collective phenomenon of superconducting phase transition, where the self-consistent construction of the electron pair wave function should be performed. Then a tight-binding-like treatment for the description of the electronic structure might be possible using the geminal of the time-reversal electron pair as the fundamental entity of the Wannier function. In this connection, that the effective charge should not exceed Z_c is considered to be the atomic-like foundation of the general belief that the Cooper pair is composed of electrons in the very vicinity of the Fermi surface. Indeed, electrons moving closer to the nucleus should feel larger positive charge of the nucleus, so that if the effective Z exceeds Z_c then the stabilization of the time-reversal electron pair is not expected at all. Only those electrons moving farther from the nucleus feel the effective Z smaller than Z_c, and hence deserves to be paired. Moreover, if the medium becomes more homogeneous, which is the case of conventional metallic superconductors, then the overlap of the time-reversal electron pair is further developed, where the coherence length becomes large.

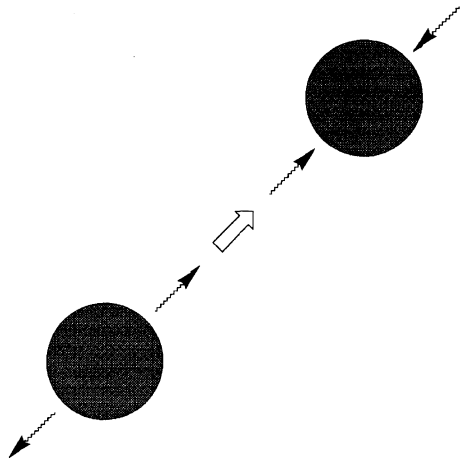

Fig. 9. If time is reversed, the outgoing wave of the electron pair changes to the incoming wave. This situation occurs on the scattering center and in between the adjacent scattering centers.

It should be noted that our discussion is not in a position to deny the other possible mechanisms that are responsible for the creation of the time-reversal pair.[10] Instead, our analysis guarantees the "stabilization" of the time-reversal pair that is created by any means: once the time-reversal pair is created, our analysis displays the criterion by which the time-reversality is preserved.

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