Excitation transfer between atoms

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The physical picture of excitation transfer between atoms is investigated. A characteristic function is introduced to make the field description complete. It is shown that such quantities as the radiation-field intensity and energy, the atomic-electron velocity, coordinates, and energies, vary in a retarded fashion. The change of the energy of an initially unexcited atom is calculated in fourth-order perturbation theory. It is also shown that the matrix element previously used as a measure of excitation transfer is strictly speaking not such a measure so that the retardation requirement is not applicable to it. By the same token, the nonretarded behavior of this matrix element, which was established by a number of workers, finds a natural explanation.

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In his known 1932 paper,¹ devoted to the development of quantum electrodynamics, Fermi investigated the propagation of excitation from one atom to another. The considered atoms were spaced a distance R apart, in the entire atoms + field system was described by a Hamiltonian H and was at t=0 in a state $|ab0\rangle$: the first atom in the ground state, the second in an excited state, and photons were absent. To describe the excitation transfer, Fermi used the square of the modulus of the matrix element

$$\mathbf{M} = \langle ba0 | e^{-iHt} | ab0 \rangle \quad (\hbar = 1), \tag{1}$$

representing the probability of observing the system at the instant t>0 in the state $|ba0\rangle$ with the first atom excited, the second unexcited, and zero photons. This matrix element was used as a measure of excitation transfer in most subsequent papers²⁻⁵ dealing with this question. Fermi has shown that the matrix element M is equal to zero up to the instant t=R/c.

This result, however, was approximate, and a more accurate calculation^{6.7} has shown that the matrix element M contains a small additional part which is not equal to zero prior to the instant t=R/c. Since one can expect any quantity that characterizes excitation transfer to have a delay R/c, as follows from elementary relativistic considerations, the presence in M of an additional nonretarded part is a paradox that calls for clarification.

It is shown in the present paper that the matrix element M is strictly speaking not a measure of excitation transfer between atoms, so that one should expect no retardation from it. On the other hand, transfer of excitation must be characterized by a change in the average values of the dynamic variables, such as the coordinate, velocity, electron energy, and others. It is shown by the the same token that, despite the absence of a retardation in the matrix element M, the excitation transfer between atoms proceeds in causal fashion.

The formulation of the problem in this paper is the same as in Ref. 1. We investigate, however, not the matrix element M, but the change in the mean values of the dynamic parameters at different points of the investigated system.

Assume that at the initial instant of time t=0 the system is in the state $|ab0\rangle$, i.e., the first atom is not ex-

cited, the second is excited, and there are no photons. It will be shown that although only the second atom is excited initially, both atoms are centers of electromagnetic-field radiation. As for the second atom, it radiates because it is excited. The first atom, on the other hand, is a source of radiation by virtue of the fact that its ground state $|a\rangle$ is not an eigenstate of the complete Hamiltonian. It begins to interact from the very outset with the oscillations of the vacuum, goes over into the lowerlying ground state of the entire system, and radiates.

A similar situation for a free electron was considered by Ginzburg.⁸ Naturally, the emission of the first atom is much less than that of the second. It can be shown that the radiation fronts are abrupt—their smearing is of the order of the dimensions of the atom, and the propagation of these fronts proceeds in retarded fashion. At sufficiently short times, before these fronts intersect, the space between them is in the same excited state as at the initial instant. This means that "nothing slipped-in" in that time between the atoms, and the difference of the matrix element M from zero at these instants of time is due to some other causes, but not to the excitation transfer from one atom to the other. It is precisely this circumstance which shows that the matrix element M, strictly speaking, cannot be a measure of the excitation transfer between atoms.

It will also be shown that excitation of the first atom, which was initially unexcited, is due to other causes. From the very outset, the first atom interacts with the oscillations of the vacuum and with the Coulomb field of the second atom. This interaction leads to a certain development of its state and to the appearance in it of an admixture of an excited state. The first atom interacts also with the radiation field of the second atom. The excitation of the first atom due to this cause is strictly retarded. This proves that the excitation propagation is causal.

At the same time, the fact that the states of both atoms change from the very beginning explains the nonretardation of the matrix element M. Indeed, the latter contains the coordinates of both atoms, i.e., it is the characteristic of two places in the system, both of which change starting with the instant t=0. Therefore the matrix element also changes starting with t=0.

In the investigation of the state of an electromagnetic

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field, it is convenient to use as a characteristic of the excitation of the field at a given point of space the characteristic function

$$C(\boldsymbol{\xi}, \boldsymbol{\eta}) = \langle ab0 | e^{i\boldsymbol{\xi} \mathbf{E} + i\boldsymbol{\eta} \mathbf{H}} | ab0 \rangle, \qquad (2)$$

where $\mathbf{E}(\rho)$ and $H(\rho)$ are field operators in the Heisenberg representation at the observation point ρ ; $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$ are arbitrary vectors. The value of the characteristic function lies in the fact that if it is known then, differentiating it with respect to $\boldsymbol{\xi}_{\lambda}$ and η_{λ} and putting then $\boldsymbol{\xi}$ =0 and $\boldsymbol{\eta}$ =0, we can obtain the mean value, in the state $|ab0\rangle$, of all the powers of $E_{\lambda}(\rho)$ and $H_{\lambda}(\rho)$ (λ =1,2,3) and their products. We shall assume the characteristic function to be a complete description of the field at the point ρ . In particular, it is natural to assume that if the characteristic function at a certain point of space is the same as in the vacuum state, then no electromagnetic field is excited at this point.

Thus, we consider a system of two atoms separated by a distance R. It is assumed (this is not a fundamental restriction) that each atom contains one zero-spin nonrelativistic electron. The Hamiltonian of the atoms plus field system is given by

$$H = H_s + H_r + H_t + H', \tag{3}$$

where the first three terms ($\hbar = c = 1$)

$$H_{s} = \frac{\mathbf{p}_{s}^{2}}{2m} + V(\mathbf{q}_{s}); \quad H_{T} = \frac{\mathbf{p}_{T}^{2}}{2m} + V(\mathbf{q}_{T}); \quad H_{f} = \sum_{j} k_{j} a_{j}^{+} a_{j}$$
(4)

are respectively the Hamiltonians of the first atom S, of the second atom T, and of the electromagnetic field, while their sum is the unperturbed part H_0 of the total Hamiltonian. The interaction Hamiltonian consists of the following parts:

$$H' = S + S' + T + T' + Q + V_s + V_r,$$
(5)

where

$$S = -\frac{e}{2m} \{\mathbf{p}_{s}; \mathbf{A}(\mathbf{r}_{s})\}, \quad T = -\frac{e}{2m} \{\mathbf{p}_{T}; \mathbf{A}(\mathbf{r}_{T})\},$$

$$S' = \frac{e^{2}}{2m} \mathbf{A}^{2}(\mathbf{r}_{s}), \quad T' = \frac{e^{2}}{2m} \mathbf{A}^{2}(\mathbf{r}_{T}),$$

$$Q = \frac{e^{2}}{|\mathbf{r}_{s} - \mathbf{r}_{T}|} = \frac{e^{2}}{|\mathbf{r}_{sT}|}, \quad V_{s} = \frac{-e^{2}}{|\mathbf{R} - \mathbf{r}_{s}|}, \quad V_{T} = \frac{-e^{2}}{|\mathbf{r}_{T}|},$$

$$\mathbf{r}_{s} = \mathbf{q}_{s}, \quad \mathbf{r}_{T} = \mathbf{R} + \mathbf{q}_{T}, \quad \mathbf{r}_{sT} = \mathbf{r}_{s} - \mathbf{r}_{T}.$$
(6)

The system considered is at the initial instant of time in a state $|ab0\rangle$, which is an eigenstate of the unperturbed Hamiltonian H_0 .

Such an initial condition is universally accepted in problems of this type. Sometimes the discussion of the excitation transfer focuses precisely on the choice of the initial state. It is assumed that if it is successfully chosen the matrix element M will work well. However, excitation transfer can take place under various initial conditions, but not under some exclusive ones. A reasonable measure of excitation transfer should be suitable for a large class of initial conditions, including the one used in the present paper.

Any Heisenberg operator C(t) can be expanded in a series

$$C(t) = C_t + (-i) \int_0^t dt_1 [C_i; H_1'] + (-i)^2 \int_0^t dt_2 \int_{t_1}^t dt_1 [[C_i; H_1']; H_2'] + \dots, \quad (7)$$

which we shall use hereafter and in which H'_{α} ($\alpha=1, 2, \ldots$) is the Hamiltonian of the interaction in the interaction representation while the index α denotes the time on which the Hamiltonian depends; C_t is the operator C in the interaction representation, and depends on the time t. The lower limit of integration in this expansion is set equal to zero in accordance with the problem with the initial condition at t=0.

The characteristic function of the electromagnetic field. The main difficulty in the calculation of the characteristic function (2) it is due to the Coulomb gauge assumed by us. In this gauge, the electric field **E** breaks up into two parts: a transverse part \mathbf{E}^{\perp} and a longitudinal Coulomb field \mathbf{E}^{\parallel} . The change of the Coulomb field is instantaneous in all of space. The transverse part of the field also contains an instantaneous term, which when \mathbf{E}^{\perp} is added to the Coulomb field \mathbf{E}^{\parallel} is cancelled out when the latter changes. This distinguishing feature of the Coulomb gauge is well known.⁹⁻¹¹

Using the expansion (7), we represent the transverse part of the electric field in the form of the series

$$\mathbf{E}^{\perp}(t) = \mathbf{E}_{t}^{\perp} + (-i) \int_{0}^{t} dt_{i} [\mathbf{E}_{t}^{\perp}; H_{i}'] + (-i)^{2} \int_{0}^{t} dt_{2} \int_{r_{2}}^{t} dt_{i} [[\mathbf{E}_{t}^{\perp}; H_{i}']; H_{2}'] + \dots,$$
(8)

where

$$\mathbf{E}_{i}^{\perp} = i \sum_{j} (2\pi k_{j})^{\prime j} \mathbf{e}_{j} (a_{j} e^{i\mathbf{k}_{j}p - i\mathbf{k}_{j}t} - a_{j}^{+} e^{-i\mathbf{k}_{j}p + i\mathbf{k}_{j}t}).$$

Taking (5) into account, we write down the commutator $[E_t^{i}; H_1']$, which is contained in each term of the series (8), in the form

$$[\mathbf{E}_{t}^{\perp}; H_{i}'] = [\mathbf{E}_{t}^{\perp}; S_{i} + S_{i}'] + [\mathbf{E}_{t}^{\perp}; T_{i} + T_{i}'] = \mathbf{K}_{s_{i}} + \mathbf{K}_{T_{i}}$$

We confine ourselves to calculation of K_{S_1} . An expression for K_{T_1} is obtained by replacing in the corresponding formulas the subscript S by T. With the aid of (6) we obtain the expression

$$\mathbf{K}_{s_{1}} = -\frac{e}{2m} \sum_{\lambda_{\mu}} \mathbf{e}_{\lambda} \{ (p_{s_{1}}^{\mu} - eA_{s_{1}}^{\mu}); [E_{t}^{\perp\lambda}; A_{s_{1}}^{\mu}] \},$$
(9)

where the subscript 1 of the operators p_{S_1} and A_{S_1} means that in the interaction representation they depend on the time t_1 . Dividing the commutator in (9) into a retarded part and an instantaneous part¹¹ we obtain for K_{S_1} also two parts: retarded

$$\mathbf{K_{s_1}}^{R} = \frac{ie}{2m} \operatorname{rot} \operatorname{rot} \left\{ \left(\mathbf{p}_{s_1} - e\mathbf{A}_{s_1} \right); \frac{\theta(\tau - \rho_{s_1})}{\rho_{s_1}} \right\} - \frac{2\pi ie}{m} \left\{ \left(\mathbf{p}_{s_1} - e\mathbf{A}_{s_1} \right); \delta(\boldsymbol{\rho}_{s_1}) \right\},$$
(10)

which is equal to zero at $0 < \tau \rho_{S1}$, and instantaneous

$$\mathbf{K}_{s_1}' = [H_1; \mathbf{E}_{s_1}^{"}]; \quad \mathbf{E}_{s_1}^{"} = -\operatorname{grad} \frac{e}{\rho_{s_1}},$$
 (11)

where \mathbf{E}_{S_1} is the Coulomb field of the electron of the atom S. We write down together the instantaneous terms of the series (8)

$$\mathbf{E}_{t}^{\perp} + (-i) \int_{0}^{t} dt_{1} \left\{ (\mathbf{K}_{s_{1}}{}^{t} + \mathbf{K}_{\tau_{1}}{}^{t}) + (-i) \int_{0}^{t_{1}} dt_{2} [(\mathbf{K}_{s_{1}}{}^{t} + \mathbf{K}_{\tau_{1}}{}^{t}); H_{2}{}^{t}] + \ldots \right\}^{t}.$$

The sum in the curly brackets can be convoluted with the aid of the expansion (7). Then, taking (11) into account, we obtain for the instantaneous part of the series (8) the expression

$$\mathbf{E}_{t}^{\perp} - \int_{0}^{t} dt_{1} \left[\frac{d\mathbf{E}_{s}^{\parallel}}{dt_{1}} + \frac{d\mathbf{E}_{r}^{\parallel}}{dt_{1}} \right] = \mathbf{E}_{t}^{\perp} - \mathbf{E}_{s}^{\parallel}(t) + \mathbf{E}_{s}^{\parallel}(0) - \mathbf{E}_{r}^{\parallel}(t) + \mathbf{E}_{r}^{\parallel}(0).$$

It is easily seen that in the calculation of the total electric field the terms $\mathbf{E}_{S}^{"}(t)$ and $\mathbf{E}_{T}^{"}(t)$, which represent the instantaneous Coulomb fields of the electrons of the atoms, cancel out and the electric-field operator takes the form

$$\mathbf{E}(t) = \mathbf{E}_{t}^{\perp} + \mathbf{E}_{s}^{\parallel}(0) + \mathbf{E}_{r}^{\parallel}(0) + (-i) \int_{0}^{0} dt_{1} (\mathbf{K}_{s_{1}}^{R} + \mathbf{K}_{r_{1}}^{R}) + (-i)^{2} \int_{0}^{i} dt_{2} \int_{t_{1}}^{i} dt_{1} [(\mathbf{K}_{s_{1}}^{R} + \mathbf{K}_{r_{1}}^{R}); H_{2}'] + \dots, \qquad (12)$$

where according to (10) all the series terms containing $\mathbf{K}_{S_1}^{R}$ are equal to zero at $t \le \rho_{S_1}$ and produce the radiation wave of the atom S. However, until it is averaged over the states, ρ_{S_1} is not yet defined. The terms containing $\mathbf{K}_{T_1}^{R}$ correspond to the radiation wave of the second atom. The fields $\mathbf{E}_{S}^{\parallel}(0)$ and $\mathbf{E}_{T}^{\parallel}(0)$ are the Coulomb fields of the atoms that exist in space at the instant of the start of the radiation. Similar but simpler (because of the absence of a longitudinal part) calculations for a magnetic field lead to the following retarded expression:

$$\mathbf{H} = \mathbf{H}_{i} + (-i) \int_{0}^{i} dt_{1} (\mathbf{L}_{s_{1}} + \mathbf{L}_{\tau_{1}}) + (-i)^{2} \int_{0}^{i} dt_{2} \int_{t_{2}}^{i} dt_{1} [(\mathbf{L}_{s_{1}} + \mathbf{L}_{\tau_{1}}); H_{2}'] + \dots,$$
(13)

where

$$\mathbf{L}_{s_1} = \frac{ie}{2m} \operatorname{rot} \left\{ \left(\mathbf{p}_{s_1} - e\mathbf{A}_{s_1} \right); \frac{\delta(\tau - \rho_{s_1})}{\rho_{s_1}} \right\}$$

and L_{T1} is obtained by replacing the subscript S by T.

We now investigate the characteristic function (2). To this end we substitute (12) and (13) in (2). We expand next the exponential in a series and group separately the terms containing the integrals with respect to time from (12) and (13), and those not containing such integrals. We denote them respectively by ΔC and C_0

 $C = C_0 + \Delta C$.

The quantity C_0 , as will be shown below, is none other than the initial characteristic-function value that describes the electromagnetic field at some point of space prior to the arrival of the electromagnetic wave at this point. Indeed, by definition

 $C_{0} = \langle ab0 | \exp \{ i [\xi \mathbf{E}_{t} + \eta \mathbf{H}_{t} + \xi \mathbf{E}_{s} | (0) + \xi \mathbf{E}_{r} | (0)] \} | ab0 \rangle,$

recognizing that

 $\mathbf{E}_t^{\perp} = e^{iH_f t} \mathbf{E}^{\perp}(0) e^{-iH_f t}, \qquad \mathbf{H}_t = e^{iH_f t} \mathbf{H}(0) e^{-iH_f t},$

we obtain

 $C_{\mathfrak{s}} = \langle ab0 | \exp \{ i [\xi \mathbf{E}^{\perp}(0) + \eta \mathbf{H}(0) + \xi \mathbf{E}_{\mathfrak{s}}^{\parallel}(0) + \xi \mathbf{E}_{\mathfrak{r}}^{\parallel}(0)] \} | ab0 \rangle.$

Consequently, prior to the arrival of the wavefront at some point of space, the electromagnetic field at this point is characterized by the initial Coulomb field and by the initial vacuum fluctuations of various orders.

We consider now a typical term contained in ΔC :

$$\boldsymbol{\xi} \langle b0| \int_{0}^{1} dt_{2} \int_{t_{1}}^{1} dt_{1} [\mathbf{K}_{T1}^{R}; T_{2}'] | b0 \rangle.$$
(14)

Since K_{T1}^{R} contains a retarded function, it can be inter-

preted as the summation of the radiation coming from those points of the atom T, which produce at the instant t a field at the observation point. The problem is made simpler by the fact that the electron moves in the atom slowly and is only slightly displaced during the time of passage of the front over the atom. Consequently the atomic operators in (14) can be taken in the Schrödinger equation and not in the interaction representation. It becomes clear then that in (14) and in similar expressions contributions are made only by those ρ_T which land in the volume occupied by the atom in the initial state $|b\rangle$. Consequently, up to the instant of time $t = \rho - a$, where a is the Bohr radius, the term ΔC will be exponentially small, and after that instant it will grow during the time 2a. This means that the change of the characteristic function is retarded, and the smearing of the front is of the order of the dimensions of the atom. It is easily understood also that this front is spherical, inasmuch as only the modulus ρ_T figures everywhere.

Thus, until the radiation front of one of the atoms reaches the observation point, the electromagnetic field at this point is in the same state as at the initial instant of time.

Excitation transfer between atoms. The most complete description of the transfer of excitation to an unexcited atom is given by the change of its characteristic function

 $C(\boldsymbol{\xi}, \boldsymbol{\eta}) = \langle ab0 | \exp(i\boldsymbol{\xi} \mathbf{r}_s + i\boldsymbol{\eta} \dot{\mathbf{r}}_s) | ab0 \rangle.$

It is difficult, however, to compare this function with the known results. We shall therefore calculate the average energy of the electron of the first atom. As we shall see later, the change of this energy, due to the excitation transfer, is approximately equal to the product of $|M|^2$ by the energy difference between the excited and unexcited states. This explains why the use of $|M|^2$ as a measure of the transfer has not led for a long time to any difficulties.

In the calculation we encounter terms of three types. First, terms that do not contain the coordinates of the second atom T. The retardation requirement does not apply to them. In accordance with their physical meaning, we shall call them the self-action terms and will not consider them in detail. The terms of the second type are the retarded terms due to radiation of the second atom T. Finally, the terms of the third type are connected in one manner or another with the Coulomb field. Physically, the second atom can influence the first atom prior to the instant t=R only by its initial Coulomb field. Therefore these terms should be grouped ultimately in such a way that the coordinates of the second atom are contained in them only at the initial instant of time t=0.

Local and nonlocal variables. Before we proceed to concrete calculations, we discuss the question of the local and nonlocal variables. Local variables characterize some concrete point of the considered system, whereas the nonlocal variables characterize the entire system as a whole or some extended part of the system. Accordingly, we can require retardation of the local variables is signals propagate in the systems. For the nonlocal variables the retardation requirement is either not applicable or is applicable with some restriction or another. The foregoing can be illustrated with coupled spatially separated mechanical oscillators as an example. It is known that such a system can be described in two ways. Either with the aid of the coordinates and momenta of the individual oscillators-these are obviously the local variables; the other possible description is provided by the normal oscillations, their amplitudes, and the corresponding generalized momenta. It is perfectly clear that the normal oscillations characterize the system as a whole. The amplitudes and the momenta of the normal oscillations are nonlocal, although they are canonical Hamiltonian variables. We cannot demand of them retardation when signals propagate in the system. In a consistent quantum field-theoretical approach, the amplitudes of the fields are assumed by definition to be local variables. From this follows, in particular, the condition that the commutator of such quantities vanish at points separated by a space-like interval.

We turn now to the variables \mathbf{r}_s and $\dot{\mathbf{r}}_s$. We assume that the variable \mathbf{r}_s is local. In essence, we assume this without proof, although this seems clear intuitively. Then the velocity $\dot{\mathbf{r}}_s$ should also be regarded as local. We now consider the canonical momentum \mathbf{p}_s . It is known to be equal to

 $\mathbf{p}_s = m\dot{\mathbf{r}}_s + e\mathbf{A}(\mathbf{r}_s).$

The first quantity in this sum is local. The second, on the other hand [the vector potential $\mathbf{A}(\mathbf{r}_s)$ in the Coulomb gauge] cannot be regarded as a local quantity. In fact, as we have already indicated, $\mathbf{A}(\mathbf{r}_s)$ contains an instantaneous part and consequently is not retarded and cannot be a local variable. This is evidenced by the presence of an instantaneous part in the commutator of the components of the vector potential. Therefore the generalized momentum \mathbf{p}_s can likewise not be regarded as local and consequently the different generalized-momentum functions are not retarded quantities. Thus, it is natural to require retardation of \mathbf{r}_s and $\dot{\mathbf{r}}_s$ and of different functions of them.

The energy of the first atom is not an integral of the motion. It can therefore be determined only accurate to the energy of the interaction. We assume the energy of the interaction. We assume the energy of the electron of the first atom to be the operator

 $E_s = \frac{1}{2}m\dot{\mathbf{r}}_s^2 + V(\mathbf{r}_s).$

This choice is governed by the fact that the energy must be a function of the local variables r_s and $\dot{\mathbf{r}}_s$, but not of r_s and p_s .

Using the expansion (7) and recognizing that E_s in the interaction representation contains terms of zeroth, first, and second order in e, we obtain a zeroth order only the constant term H_s . The two terms of first order der

 $(-i)\int dt_{i}[H_{s}; S_{i}]$ and S_{i}

are obviously self-action terms. In second order, discarding the interaction, we have the following terms:

$$(-i)^{2}\int_{0}^{1} dt_{2} \int_{t_{1}}^{1} dt_{1}[[H_{s}; S_{1}]; T_{2}] + (-i) \int_{0}^{1} dt_{1}[H_{s}; Q_{11}] + (-i) \int_{0}^{1} dt_{1}[S_{i}; T_{1}].$$

(15) We represent the first term of (15) in the form of two terms:

$$(-i)^{2} \int_{t_{1}}^{t_{2}} dt_{2} \int_{t_{1}}^{t_{1}} dt_{1} [[H_{s}; S_{1}]; T_{2}] - i \int_{t_{2}}^{t_{1}} dt_{2} [S_{i}; T_{2}] + (-i) \int_{t_{1}}^{t_{1}} dt_{2} \int_{t_{1}}^{t_{1}} dt_{1} [S_{i}; T_{2}],$$

where the dot denotes the partial derivative with respect to the time t_1 , which enters in the photon creation and annihilation operators in the interaction representation. The first term in it is cancelled by the third term of (15). We divide the second term into an instantaneous part

$$\int_{0}^{1} dt_{2} \int_{t_{1}} dt_{1} \frac{d^{2}Q_{12}}{dt \ dt} = i \int_{0}^{1} dt_{1} \left([H_{s}; Q_{11}] - [H_{s}; Q_{10}] \right),$$
(16)

where $Q_{12} = e^2 / |r_{S_1} - r_{T2}|$, and a retarded part

$$(-i)\int_{0}^{\infty} dt_{2}\int_{t_{2}}^{t_{1}} dt_{1} \alpha_{12}^{R}$$

where

$$\alpha_{12}^{R} = -i\left(\frac{e}{2m}\right)^{2} \sum_{\lambda\mu} \left\{ p_{S1}^{\lambda}; \left\{ p_{T2}^{\mu}; \widehat{W}_{\lambda\mu} - \frac{\tau_{12} - r_{ST}}{r_{ST}} \Theta(\tau_{12} - r_{ST}) + 4\pi \tau_{13} \delta_{\lambda\mu} \delta(\mathbf{r}_{ST}) \right\} \right\}$$
$$\widehat{W}_{\lambda\mu} = \delta_{\lambda\mu} \Delta_{r_{S}} - \frac{\partial^{2}}{\partial r_{S0}}, \quad \tau_{12} = t_{1} - t_{2}, \quad \mathbf{r}_{ST} = \mathbf{r}_{S1} - \mathbf{r}_{T2}.$$

It is easily seen that the first term of the instantaneous part in (16) is cancelled by the second term of (15). We thus obtain in second order the expression

$$E_{s}^{(2)} = (-i) \int_{0}^{t} dt_{2} \int_{0}^{t} dt_{1} \alpha_{12}^{R} + (-i) \int_{0}^{t} dt_{1} [H_{s}; Q_{10}], \qquad (17)$$

the first term of which is retarded and the second instantaneous. However, it contains the coordinates of the electron of the atom T, taking only at the zeroth instant of time, and corresponded to the initial Coulomb field of the second atom. Therefore the presence of this term does not violate the retarded character of the electron motion.

In third-order perturbation theory, all the terms vanish upon averaging over the vacuum state, since they contain only odd powers of the vector potential. We have also performed calculations in fourth order and have shown that the energy change of the electron of the first atom at $0 \le t \le R$ is determined by the initial Coulomb field and by self-action. At $t \ge R$ there are added to these terms retarded terms due to the radiation of the second atom. For large distances $R \gg \lambda$ between the atoms and at $\lambda \gg a$, where λ is the radiation wavelength and a is the Bohr radius, these terms simplify and the retarded part of the energy change of the first atom is given by

$$E_{ba}^{(8)}\left|(-i)^{2}\int_{0}^{t}dt_{2}\int_{t_{a}}^{1}dt_{1}\langle ba|\alpha_{12}^{R}|ab\rangle\right|^{2} (E_{ba}^{(8)}=E_{b}^{(8)}-E_{a}^{(8)}), \quad (18)$$

in the calculation of which it is necessary to neglect all the terms that decrease with distance like the Coulomb terms. The detailed calculations in fourth order, which we do not present for lack of space, can be found in Ref. 12. At equal resonant energies of the atoms, $E_{ba}^{(S)} = E_{ba}^{(T)} = \hbar \omega_0$, the energy change takes the form

$$\Delta E = \hbar \omega_0 \left| \alpha \left[\left(\mathbf{d}_{ba}^{s} \mathbf{d}_{ab}^{\tau} \right) - \left(\mathbf{d}_{ba}^{s} \hat{\mathbf{R}} \right) \left(\mathbf{d}_{ab}^{\tau} \hat{\mathbf{R}} \right) \right] \frac{\omega_n^2 (t - R/c)}{cR} \right|^2 \theta \left(t - \frac{R}{c} \right),$$

where α is the fine-structure constant, $\hat{\mathbf{R}} = \mathbf{R}/|\mathbf{R}|$, and \mathbf{d}_{ba} is the matrix element of the coordinates of the electrons. This energy change coincides with the product $\hbar\omega_0$ by the square of the modulus of the matrix element M, calculated in Refs. 3 and 4 in the region

 $\omega_0^{-1} \ll t - R/c \ll \tau_s, \ \tau_\tau,$

where τ_s and τ_r are the lifetimes of the atoms in the excited states. However, this quantitative agreement is accidental; the matrix element M, first introduced by Fermi,¹ is not retarded, in contrast to the change of the energy of the first atom, and cannot serve as a measure of excitation transfer.

Conclusion. The main result of our paper is a clarification of the physical picture of excitation transfer between two atoms. We have established that the process has a retarded character.

It was shown in this paper that the matrix element M, strictly speaking, is not a measure of the excitation transfer from one atom to another, therefore one cannot require it to be subject to retardation. It would be correct to state that M is a correlator of states at two different points. The retardation, on the other hand, can be required only of a quantity that characterizes either point of space, but only one of them. An investigation of the characteristic function of the electromagnetic field has shown that a radiation produces near each atom spherical wavefronts, and the space between these fronts is in the same state as before the start of the radiation. This means that nothing has been physically transferred from one atom to the other prior to this instant.

We have investigated the energy of an initially excited atom with accuracy to fourth order of perturbation theory. We have shown that its change, due to the motion of the second atom, has a retarded character. For the energy change in fourth order we obtain practically the same expression as in Fermi's paper, but multiplied by $E_{ba}^{(S)}$ and, of course, retarded. However, the change of the energy of the first atom, due to the excitation transfer (17), takes place already in second order in e, whereas according to the Fermi theory the probability of excitation transfer is a quantity of fourth order in e. To be sure, if the radiation wavelength is much larger than the size of the atom, this change (in second order) is small, as is seen from the fact that it is equal to zero in the dipole approximation.

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