

**Relativistic many-body theory of atomic transitions.
The relativistic equation-of-motion approach**

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An equation-of-motion approach is used to develop the relativistic many-body theory of atomic transitions. The relativistic equations of motion for transition matrices are formulated with the use of techniques of quantum-field theory. To reduce the equations of motion to a tractable form which is appropriate for numerical calculations, a graphical method to resolve the complication arising from the antisymmetrization and angular-momentum coupling is employed. The relativistic equation-of-motion method allows an *ab initio* treatment of correlation and relativistic effects in both closed- and open-shell many-body systems. A special case of the present formulation reduces to the relativistic random-phase approximation.

I. INTRODUCTION

Treatment of relativistic and correlation effects in many-particle systems has become essential in many fields of physics. We introduce a relativistic equation-of-motion approach¹ to deal with these two effects in an *ab initio* manner.

In Sec. II we define the transition matrix in the quantum-field theory and derive equations of motion for transition matrices. Section III gives the transition amplitudes in terms of transition matrices. The kinematic structure of transition matrices can be obtained by a graphical prescription² given in Sec. IV. In Sec. V, we demonstrate the solution of the relativistic equations of motion by giving a simple example which reduces to the relativistic random-phase approximation (RRPA).³ The present formulation is, however, more general and can treat both open- and closed-shell systems. In addition, multiexcitations can be taken into account. Relativistic equations of motion for a many-particle system with general *n*-particle interactions can also be derived. These and detailed treatment of open-shell systems are given in a separate paper.⁴

II. EQUATIONS OF MOTION FOR TRANSITION MATRICES

For many-fermion systems, the creation and annihilation operators satisfy the anticommutation relations

$$\{c_i, c_j^\dagger\} = \delta_{ij}, \tag{1}$$

$$\{c_i, c_j\} = \{c_i^\dagger, c_j^\dagger\} = 0, \tag{2}$$

where the curly brackets denote the anticommutation relation. The field operators are given by

$$\psi_\alpha(\vec{x}, t) = \sum_i u_{\alpha i}(\vec{x}, t) c_i, \tag{3}$$

$$\psi_\alpha^\dagger(\vec{x}, t) = \sum_i u_{\alpha i}^\dagger(\vec{x}, t) c_i^\dagger, \tag{4}$$

where α is used to accommodate fields with more than one component and u_i form a complete orthonormal set. The anticommutation relations of field operators are

$$\{\psi_\alpha(\vec{x}, t), \psi_\beta^\dagger(\vec{x}', t)\} = \delta_{\alpha\beta} \delta^3(\vec{x} - \vec{x}'), \tag{5}$$

$$\{\psi_\alpha(\vec{x}, t), \psi_\beta(\vec{x}', t)\} = \{\psi_\alpha^\dagger(\vec{x}, t), \psi_\beta^\dagger(\vec{x}', t)\} = 0. \tag{6}$$

For brevity, we write

$$\{\psi(\vec{x}, t), \psi^\dagger(\vec{x}', t)\} = \delta^3(\vec{x} - \vec{x}'), \tag{7}$$

$$\{\psi(\vec{x}, t), \psi(\vec{x}', t)\} = \{\psi^\dagger(\vec{x}, t), \psi^\dagger(\vec{x}', t)\} = 0 \tag{8}$$

with the variable α implied.

A general many-fermion state is given by

$$|\Psi\rangle = \sum_{ij\dots} A_{ij\dots} c_i^\dagger c_j^\dagger \dots |0\rangle, \tag{9}$$

where the coefficients $A_{ij\dots}$ in general involve coupling coefficients. The equations of motion for the field operators are

$$i \frac{\partial \psi(\vec{x}, t)}{\partial t} = [\psi(\vec{x}, t), H], \tag{10}$$

$$i \frac{\partial \psi^\dagger(\vec{x}, t)}{\partial t} = [\psi^\dagger(\vec{x}, t), H], \tag{11}$$

where H is the total Hamiltonian, and the square brackets denote the commutation relation. The total Hamiltonian H is assumed to have the form

$$H = \int d^3x_1 \psi^\dagger(\vec{x}_1, t) h(\vec{x}_1) \psi(\vec{x}_1, t) + \frac{1}{2} \int d^3x_1 \int d^3x_2 \psi^\dagger(\vec{x}_1, t) \psi^\dagger(\vec{x}_2, t) v(\vec{x}_1, \vec{x}_2) \psi(\vec{x}_2, t) \psi(\vec{x}_1, t), \quad (12)$$

where $h(\vec{x}_1)$ stands for a sum of all one-particle operators and $v(\vec{x}_1, \vec{x}_2)$ for all two-particle operators. Although three-particle and, in general, many-particle operators can be included,⁴ we will deal only with the form (12). For brevity we write Eq. (12) as

$$H = \int d^3x_1 \psi^\dagger(1) h(1) \psi(1) + \frac{1}{2} \int d^3x_1 \int d^3x_2 \psi^\dagger(1) \psi^\dagger(2) v(12) \psi(2) \psi(1). \quad (13)$$

The n th-order transition matrix is defined as

$$\Gamma_{fi}(1, \dots, n; 1', \dots, n') = \frac{1}{n!} \langle \Psi_i | \psi^\dagger(1') \cdots \psi^\dagger(n') \psi(n) \cdots \psi(1) | \Psi_f \rangle, \quad (14)$$

where i and f denote two general states of the many fermion system. In the usual application, Ψ_i and Ψ_f are states with well-defined angular momentum given in the form of Eq. (9). We can easily show that $\Gamma_{fi}(1, \dots, n; 1', \dots, n')$ is Hermitian, antisymmetric, and satisfies the recurrence relation

$$\Gamma_{fi}(1, \dots, n; 1', \dots, n') = \left[\frac{n+1}{N-n} \right] \int d^3x_{n+1} \Gamma_{fi}(1, \dots, n+1; 1', \dots, n+1'). \quad (15)$$

In Eqs. (14) and (15), the primes are introduced for purely notational purposes so that operators, if any, to the left will only operate on unprimed coordinates. However, as far as the integration is concerned, the primed and unprimed coordinates are treated as if they were the same. These will become clear later.

Assume that two states of an N -fermion system satisfy the equations

$$i \frac{\partial}{\partial t} \langle 1, \dots, N | \Psi_i \rangle = E_i \langle 1, \dots, N | \Psi_i \rangle, \quad (16)$$

$$i \frac{\partial}{\partial t} \langle 1, \dots, N | \Psi_f \rangle = E_f \langle 1, \dots, N | \Psi_f \rangle, \quad (17)$$

where E_i and E_f are total energies of Ψ_i and Ψ_f , respectively. We can show that the transition matrix between i and f states satisfies

$$i \frac{\partial}{\partial t} \Gamma_{fi}(1, \dots, N; 1', \dots, N') = \omega_{fi} \Gamma_{fi}(1, \dots, N; 1', \dots, N'), \quad (18)$$

where $\omega_{fi} = E_f - E_i$. By integrating successively over the coordinates \vec{x}_i and by applying the recurrence relation (15), we obtain, in general,

$$i \frac{\partial}{\partial t} \Gamma_{fi}(1, \dots, n; 1', \dots, n') = \omega_{fi} \Gamma_{fi}(1, \dots, n; 1', \dots, n'). \quad (19)$$

This is called the *equation of motion* for the n th-order transition matrix.

The equation of motion (19) can be written in terms of the total Hamiltonian H by using the equations of motion (10) and (11) satisfied by the field operators. The left-hand side of Eq. (19) can then be reduced to

$$\begin{aligned} i \frac{\partial}{\partial t} \Gamma_{fi}(1, \dots, n; 1', \dots, n') &= \frac{1}{n!} i \frac{\partial}{\partial t} \langle \Psi_i | \psi^\dagger(1') \cdots \psi^\dagger(n') \psi(n) \cdots \psi(1) | \Psi_f \rangle \\ &= \frac{1}{n!} \langle \Psi_i | [\psi^\dagger(1'), H] \psi^\dagger(2') \cdots \psi^\dagger(n') \psi(n) \cdots \psi(1) | \Psi_f \rangle \\ &\quad + \frac{1}{n!} \langle \Psi_i | \psi^\dagger(1') [\psi^\dagger(2'), H] \psi^\dagger(3') \cdots \psi^\dagger(n') \psi(n) \cdots \psi(1) | \Psi_f \rangle + \cdots \\ &\quad + \frac{1}{n!} \langle \Psi_i | \psi^\dagger(1') \cdots \psi^\dagger(n') \psi(n) \cdots \psi(3) [\psi(2), H] \psi(1) | \Psi_f \rangle \\ &\quad + \frac{1}{n!} \langle \Psi_i | \psi^\dagger(1') \cdots \psi^\dagger(n') \psi(n) \cdots \psi(2) [\psi(1), H] | \Psi_f \rangle. \end{aligned} \quad (20)$$

Using the explicit form (13) and carrying out the commutation relations in (20) we can write the equation of motion (19) in coordinate-operator form:

$$\begin{aligned} & \sum_{i=1}^n h(i) \Gamma_{fi}(1, \dots, n; 1', \dots, n') - \Gamma_{fi}(1, \dots, n; 1', \dots, n') \sum_{i=1}^n h(i') \\ & + (1 - \delta_{n1}) \sum_{i < j}^n [v(ij) - v(i'j')] \Gamma_{fi}(1, \dots, n; 1', \dots, n') \\ & + (1 - \delta_{nN})(n+1) \int d^3 x_{n+1} \sum_{i=1}^n [v(i, n+1) - v(i', n+1')] \Gamma_{fi}(1, \dots, n+1; 1', \dots, n+1') \\ & = \omega_{fi} \Gamma_{fi}(1, \dots, n; 1', \dots, n'). \end{aligned} \quad (21)$$

Equation (21) is formally equivalent to the nonrelativistic equations of motion derived in the configuration space.⁵

In calculations using basis wave functions, it is more convenient to express the equations of motion in the occupation-number space. The transition matrix in the occupation-number space is defined as

$$\begin{aligned} \Gamma_{fi}^{(n)} & \equiv \frac{1}{(N-n)!} \int d^3 x_{n+1} \cdots d^3 x_N \psi(N) \cdots \psi(n+1) | \Psi_f \rangle \langle \Psi_i | \psi^\dagger(n+1') \cdots \psi^\dagger(N') \\ & = \frac{1}{(N-n)!} \sum_{j \cdots k} c_j \cdots c_k | \Psi_f \rangle \langle \Psi_i | c_k^\dagger \cdots c_j^\dagger. \end{aligned} \quad (22)$$

By applying the commutation relations (7) and (8), we can prove that Eq. (22) and the transition matrix in the coordinate space are related by

$$\Gamma_{fi}(1, \dots, n; 1', \dots, n') = \langle 1, \dots, n | \Gamma_{fi}^{(n)} | 1', \dots, n' \rangle. \quad (23)$$

A recurrence relation is satisfied by the transition matrices in the occupation-number space:

$$\Gamma_{fi}^{(n)} = \frac{1}{(N-n)} \int d^3 x_{n+1} \psi(n+1) \Gamma_{fi}^{(n+1)} \psi^\dagger(n+1'). \quad (24)$$

Following a similar procedure as before, we obtain the equation of motion in the occupation-number space:

$$h \Gamma_{fi}^{(n)} - \Gamma_{fi}^{(n)} h + (1 - \delta_{n1})(1+n-N)(v \Gamma_{fi}^{(n)} - \Gamma_{fi}^{(n)} v) + (1 - \delta_{nN}) \sum_j c_j (v \Gamma_{fi}^{(n+1)} - \Gamma_{fi}^{(n+1)} v) c_j^\dagger = \omega_{fi} \Gamma_{fi}^{(n)}, \quad (25)$$

where

$$h \equiv \int d^3 x_1 \psi^\dagger(1) h(1) \psi(1) = \sum_{kl} h_{kl} c_k^\dagger c_l, \quad (26)$$

$$v \equiv \frac{1}{2} \int d^3 x_1 \int d^3 x_2 \psi^\dagger(1) \psi^\dagger(2) v(12) \psi(2) \psi(1) = \frac{1}{2} \sum_{klmn} v_{klmn} c_l^\dagger c_k^\dagger c_m c_n. \quad (27)$$

III. TRANSITION AMPLITUDES

The most general interaction operator for an N -particle system is

$$V = \sum_{i=1}^N v(i) + \sum_{i < j}^N v(ij) + \sum_{i < j < k}^N v(ijk) + \cdots + \sum_{i < j \cdots < l}^N v(ij, \dots, l) + \cdots + v(1, \dots, N),$$

where $v(ij, \dots, l)$ denotes a general n -particle operator; i.e., i, j, \dots, l are n in number. The transition amplitude from state i to state f due to V can be written in terms of transition matrices as

$$\begin{aligned} P_{fi} & = \int d^3 x_1 v(1) \Gamma_{fi}(1; 1') + \int d^3 x_1 \int d^3 x_2 v(12) \Gamma_{fi}(12; 1'2') \\ & + \int d^3 x_1 \int d^3 x_2 \int d^3 x_3 v(123) \Gamma_{fi}(123; 1'2'3') + \cdots \\ & + \int d^3 x_1 \cdots \int d^3 x_N v(1, \dots, N) \Gamma_{fi}(1, \dots, N; 1', \dots, N'). \end{aligned} \quad (28)$$

In the occupation-number space, we have

$$\begin{aligned}
P_{fi} = & \int d^3x_1 \langle 1 | v^{(1)} \Gamma_{fi}^{(1)} | 1' \rangle + \int d^3x_1 \int d^3x_2 \langle 12 | v^{(2)} \Gamma_{fi}^{(2)} | 1'2' \rangle \\
& + \int d^3x_1 \int d^3x_2 \int d^3x_3 \langle 123 | v^{(3)} \Gamma_{fi}^{(3)} | 1'2'3' \rangle + \cdots \\
& + \int d^3x_1 \cdots \int d^3x_N \langle 1, \dots, N | v^{(N)} \Gamma_{fi}^{(N)} | 1', \dots, N' \rangle,
\end{aligned} \tag{29}$$

where an n -particle operator is defined as

$$v^{(n)} = \frac{1}{n!} \int d^3x_1 \cdots \int d^3x_n \psi^\dagger(1) \cdots \psi^\dagger(n) v(1, \dots, n) \psi(n) \cdots \psi(1). \tag{30}$$

To evaluate Eq. (28) or (29) exactly, we would have to assume a corresponding Hamiltonian

$$H = \int d^3x_1 \psi^\dagger(1) h(1) \psi(1) + \sum_{i=2}^N v^{(i)} \tag{31}$$

and obtain a hierarchy of equations⁴ similar to (21) or (25). Transition matrices of all orders are then solved and substituted in Eq. (28) or (29) to give the transition amplitude P_{fi} . Nevertheless, we will truncate the interactions up to two-particle operators as in the assumption of Eq. (13) of the total Hamiltonian. Therefore, we are primarily interested in the two lowest-order equations of (21) or (25). The third-order transition matrix is to be approximated and related to the second-order transition matrix. The two equations of motion involving the first- and second-order transition matrices can then be solved in principle.

IV. FORMS OF TRANSITION MATRICES

The kinematic structure of transition matrices can be obtained by a graphical procedure.² The prescriptions are as follows.

(i) *First Order:*

$$\Gamma_{fi}(1, 1') = \sum_{ab} (-1)^{P_{ab}} (N_a N_b')^{1/2} | q_f(a) \rangle \langle q_i'(b) |, \tag{32}$$

where the summation is over all nonvanishing pairs. Other notations have been defined elsewhere.²

(ii) *Second Order:*

$$\begin{aligned}
\Gamma_{fi}(12; 1'2') = & \sum_{(ab, cd)} \frac{1}{2} (1 - \delta_{ab} - P_{12})(1 - \delta_{cd} - P_{1'2'}) \\
& \times (-1)^{P_{ab, cd}} [N_a(N_b - \delta_{ab})N_c'(N_d' - \delta_{cd})]^{1/2} | q_f(ab) \rangle \langle q_i'(cd) |,
\end{aligned} \tag{33}$$

where the summation is over all distinct nonvanishing pairs with $a \leq b$ and $c \leq d$. Other notations in Eq. (33) have also been defined.² In the occupation-number space, we have

$$\Gamma_{fi}^{(1)} = \sum_{ab} (-1)^{P_{ab}} (N_a N_b')^{1/2} | q_f(a) \rangle \langle q_i'(b) | c_a^\dagger c_b, \tag{34}$$

$$\begin{aligned}
\Gamma_{fi}^{(2)} = & \sum_{ab, cd} \frac{1}{2} (1 - \delta_{ab} - P_{12})(1 - \delta_{cd} - P_{1'2'}) (-1)^{P_{ab, cd}} [N_a(N_b - \delta_{ab})N_c'(N_d' - \delta_{cd})]^{1/2} \\
& \times | q_f(ab) \rangle \langle q_i'(cd) | c_a^\dagger c_b^\dagger c_d c_c.
\end{aligned} \tag{35}$$

Prescriptions for obtaining higher-order transition matrices can be similarly derived.

V. SOLUTION OF THE EQUATIONS OF MOTION

To demonstrate here the solution of the equations of motion, we will consider the trivial case of closed-shell atoms and restrict ourselves to excita-

tions through one-particle operators. The initial and final states are assumed to have the forms

$$\begin{aligned}
\Psi_i = & A_0 \Psi_0 \\
& + \sum_{aJ_a 2^c} B_{aJ_a 2^c} \Psi_{[(a^{2a-1})J_{a2}(c^2)J_{a2}]_0},
\end{aligned} \tag{36}$$

$$v_b^{\text{RPA}} u_{a'\pm} = v_b^{\text{DF}} u_{a'\pm} + \sum_{b'} [(-1)^{b-b'} w(b' \mp b) + w(bb' \pm)] u_{a'\pm}, \quad (52)$$

$$v_b^{\text{DF}} u_a = [b]^2 \left[v_0(bb) u_a - \sum_k D_k(ba) v_k(ba) u_b \right], \quad (53)$$

$$w(bc) u_{a'\pm} = \frac{1}{[J]^2} C_J(aa') C_J(bc) v_J(bc) u_a + (-1)^{b+c} \sum_k A_k(aa'bc; J) v_k(ba) u_c, \quad (54)$$

$$v_k(bc) = \int_0^\infty dr_2 v_b^\dagger(2) \frac{r_2^k}{r_2^{(k+1)}} u_c(2), \quad (55)$$

for the Coulomb interaction. Here we have used the notation $[b] \equiv (2b+1)^{1/2}$, etc. A more complicated expression can be derived for interactions including the Breit interaction, etc.⁴ The angular coupling coefficients in Eqs. (53) and (54) are

$$D_k(ab) = \begin{pmatrix} a & k & b \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}^2 \Pi(l_a k l_b), \quad (56)$$

$$C_k(ab) = (-1)^{a+1/2} [ab] \begin{pmatrix} a & k & b \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \Pi(l_a k l_b), \quad (57)$$

$$A_k(abcd; J) = (-1)^{k+J} C_k(abcd) \begin{Bmatrix} a & b & J \\ d & c & k \end{Bmatrix}, \quad (58)$$

$$C_k(abcd) = (-1)^{a+d} [abcd] \times \begin{pmatrix} a & k & c \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} b & k & d \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \times \Pi(l_a k l_c) \Pi(l_b k l_d), \quad (59)$$

with the parity function

$$\Pi(akb) = \begin{cases} 1, & a+k+b \text{ even} \\ 0, & a+k+b \text{ odd} \end{cases}.$$

Equations (50) agree with the relativistic random-phase approximation (RRPA) equations.³ The present procedure can be used to derive the RRPA equations involving parity-nonconserved interactions,⁶ the multiconfiguration relativistic random-phase approximation (MCRRPA) equations,⁷ and the RRPA equations for open-shell systems. These and other applications are given in a separate paper.⁴

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