Many-body theory of electron scattering by excited atomic targets: Fundamental formulas

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A many-body theory of electron-impact excitation out of excited atomic states is presented. After the fundamental equations and formulas of the general theory are given, first- and second-order approximations are introduced. In the case of the first-order theory, detailed analytical formulas are also developed. The physical interpretation of the first- and second-order theories are presented with the aid of Feynman-type diagrams. Following a discussion of initial- and final-state effects, the many-body theory is also related to the distorted-wave approximation.

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I. INTRODUCTION

The study of electronic collisions with excited atomic targets is of great importance for the understanding of high-density gas discharges [1], of astrophysical plasmas [2], of ionospheric and auroral processes in planetary atmospheres [3], and of electron-beam and gas-discharged pumped lasers [4]. In spite of its great importance, relative few experimental and theoretical studies have been reported in the literature in this area. Massey and Burhop [5] in their monograph refer to a few experiments prior to 1969: that of Latyscheff and Leipunsky [6] on metastable Hg targets, that of Phelps [7] on He($2\,^3S$) targets, and that of Neynaber *et al.* [8] on He($2\,^3S$) targets. Since then, additional experimental results were reported by Wilson and Williams [9] on total cross sections for He($2\,^3S$) and He($2\,^1S$) targets; Lake and Garscadden [10] measured the $2\,^3S \rightarrow 3\,^3P$ excitation cross section for He; Mityureva and Penkin [11] measured optical excitation functions for the $2\,^3S \rightarrow 3\,^3P$ transition in He and for the $3\,^3P_{0,2} \rightarrow 4\,^3P_1$ line in Ne; Gostev *et al.* [12] measured optical excitation functions out of the $2\,^3S$ level of He to higher-lying levels; and Celotta *et al.* [13] measured the total cross section for scattering of low-energy electrons by a mixture of $^3P_0$ and $^3P_2$ metastable Ar. Most importantly, however, Müller-Fiedler *et al.* [14] reported differential cross-section (DCS) results for the excitation out of the He($2\,^3S$) level to the $2\,^3P$, $3\,^3S$, $3\,^3P$, and $3\,^3D$ levels, and to the sum of the $n=4$ levels of He. Recently optical excitation functions have been reported by Rall *et al.* [15] for transitions from He($2\,^3S$) to seven higher-lying states. From their optical excitation data, these latter authors [15] have also obtained electron-impact integrated cross-section results for the $2\,^3S \rightarrow 3\,^3P$, $3\,^3S$, and $3\,^3D$ transitions. Additional experimental studies on electron-impact excitation from metastable states of rare gases include that of Gerasimov and Petrov [16], Shaw and Jones [17], Baranov, Demidov, and Kolokolov [18], Bochkova and Moritts [19], Blagoev, Mishanov, and Popov [20], and Behnke, Deutsch, and Scheibner [21]. These latter works study the properties of after-glow plasmas and obtain information (usually rate coefficients) about a variety of electron-impact processes.

The experimental technique of electron scattering by laser-excited atomic targets, introduced in 1974 by Hertel and Stoll [22], opened new possibilities for the study of electron-impact excitation out of excited atomic targets. Hertel and co-workers [23] applied this technique to study electron-impact processes for laser-pumped Na targets. Register *et al.* [24] used the same technique to measure DCS's for numerous transitions from the $6\,^1P_1$ level of Ba, and Jaduszilwer *et al.* [25–27] and Zuo *et al.* [28] used it to study electron scattering by various excited states of Na. A recent development in this area is the use of spin-polarized incident electrons for the study of superelastic scattering from a laser-excited Na target [29–31].

On the theoretical side the situation is somewhat better. The majority of calculations refer to excitations out of the $2\,^3S$ level of He. These calculations include the Born approximation [1,32–39], the Bonham-Ochkur-Rudge approximation [40], the Glauber approximation [38,41], the Vainshtein-Presnyakov-Sobelman approximation [1], the use of the multichannel eikonal approach [42–44], the polarized-orbital approximation for elastic scattering [45–47], the distorted-wave approximation (DWA) [48,49], the two-potential modified Born approximation [50,51], the close-coupling approximation [52–54], the Bethe-Goldstone variational approach [55], and R-matrix theory calculations [56–58]. Recently a computer code was developed by Clark *et al.* [59] that allows the calculation of electron-impact cross sections in various versions of the DWA for a great variety of atomic and ionic systems. Results from this computer code for a variety of transitions in Ar and Kr were published recently [60].

The limitations of the Born, Glauber, and multichannel eikonal methods are well known and discussed by the respective authors. The major problem with these methods is that they are not able to describe spin-

exchange excitation properly, and consequently they will not be able to provide reliable results for the DCS at large angles (approximately for $\vartheta > 90°$) and for transitions that occur through spin exchange (e.g., for the $2\,^3S \rightarrow 3\,^1P$ excitation of He). The R-matrix method is able to overcome these problems; however, in the past, except for the five-state R-matrix theory, it has been implemented only for low-energy ($E \leq 30$ eV) incident electrons.

Thus it appeared to be worthwhile to formulate the many-body theory of electron scattering by excited atomic targets with closed-shell ground states. The many-body theory of elastic electron scattering by closed-shell ground-state atomic targets was formulated by Bell and Squires [61] and Namiki [62], it was first applied for e-He elastic scattering by Pu and Chang [63]. The application of the Martin-Schwinger functional differentiation formalism [64,65] in this context was suggested by Schneider, Taylor, and Yaris [66], which was used in a numerical calculation for e-He scattering by Yarlagadda *et al.* [67]. The many-body theory of electron-atom inelastic scattering out of closed-shell targets was formulated by Csanak, Taylor, and Yaris [68,69] and by Emrich [70]. The first-order version of the many-body theory (FOMBT) was applied for electron-impact excitation of He [71–74], Ar [75,76], Ne [77,78], Kr [79], and Mg [80]. A second-order many-body theory (SOMBT) for inelastic scattering was formulated by Csanak, Taylor, and Tripathy [81] that gave promising results [82] for the $2\,^3S$ excitation of He. A many-body theory for excitations out of excited states was formulated by Ficocelli Varracchio [83], but results from this theory have not been reported yet.

The purpose of the present work is to extend many-body theory for the electron-impact excitation of excited atomic targets with closed-shell ground states. The first- and second-order versions of the theory will also be presented. The many-body theory will be related to the DWA and the first-order theory will be applied in a subsequent work for electron-impact excitation out of the $2\,^3S$ and $2\,^1S$ levels of He. The term scheme of He and the two levels of interest to us here are shown in Fig. 1.

II. FUNDAMENTAL EQUATIONS AND FORMULAS OF THE THEORY

A. General formulation

The development of the many-body theory of electron-impact excitation out of excited atomic targets follows closely the one introduced for excitation out of the ground state [68,69,75]. The fundamental concepts and formulas of the many-body Green's-function technique has been summarized by Csanak, Taylor, and Yaris [69] (during the rest of the paper, we shall refer to this review article as CTY) and a glossary was given by Csanak and Taylor [84].

Tables I and II list the fundamental concepts and notations used in our theory. Throughout this report we shall use hartree atomic units.

The scattering matrix for electron scattering can be given as [69]

$$S_{nq,mp} = \langle \Psi^{(-)}_{n,q} | \Psi^{(+)}_{m,p} \rangle = \langle \Psi_n | a_q^{\text{out}} a_p^{\dagger \text{in}} | \Psi_m \rangle = \lim_{\substack{t \to \infty \\ t' \to -\infty}} \langle \Psi_n | a_q(t) a_p^{\dagger}(t') | \Psi_m \rangle \quad (1)$$

where m refers to the quantum numbers of the initial (excited) target state with state vector $|\Psi_m\rangle$, p to the quantum numbers (momentum, spin) of the initial state of the incident electron, and n and q for the final-state quantum numbers of the target, with state vector $|\Psi_n\rangle$ and scattered electron, respectively.

From Eq. (1) it follows that

$$S_{nq,mp} = \lim_{\substack{t_1 \to \infty \\ t_1' \to -\infty}} \int dr\, dr' \phi_q^*(1) \phi_p(1') X_n^m(1,1') \quad (2)$$

where

$$X_n^m(1,1') = \langle \Psi_n | T(\psi(1)\psi^{\dagger}(1')) | \Psi_m \rangle \quad (3a)$$

is the excited-state–excited-state Bethe-Salpeter amplitude and

$$\phi_p(1) \equiv \phi_p(r_1 t_1) = e^{i\mathbf{p}\cdot\mathbf{r}_1} \chi_{m_s}(\sigma_1) e^{-i\varepsilon_p t_1}$$

is a propagating free-electron state wave function, where $\chi_{m_0}(\sigma_1)$ is the Pauli spin function and $\varepsilon_p = \mathbf{p}^2/2m$ is the energy of the free electron. In obtaining Eq. (2) and Eq. (1), the following relationship between the $a_p(t)$ and $\psi(rt)$ operators has been used:

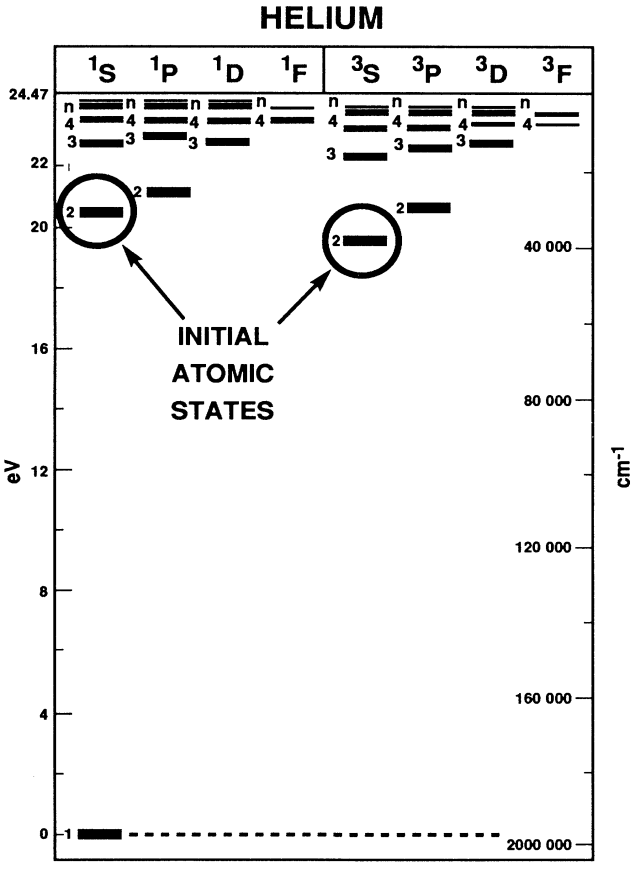

FIG. 1. The term diagram for He. The initial atomic levels of interest in this work $2\,^1S$ and $2\,^3S$ are circled.

TABLE I. Coordinates, field operators, and state vectors.

$\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\ldots$	Spatial coordinates of an electron
$\sigma,\sigma_1,\sigma_2,\ldots$	Spin coordinates of an electron
$r\equiv(\mathbf{r},\sigma),r_1\equiv(\mathbf{r}_1,\sigma_1)\cdots$	Spatial and spin coordinates of an electron
$\mathbf{p},\mathbf{p}_1,\mathbf{p}_2,\ldots$	Momentum coordinates of an electron
$p\equiv(\mathbf{p},\sigma),p_1\equiv(\mathbf{p}_1,\sigma_1)\cdots$	Momentum and spin coordinates of an electron
$t,t_1,t_2,\ldots$	Time coordinates of an electron
$1\equiv(\mathbf{r}_1,\sigma_1,t_1),2\equiv(\mathbf{r}_2,\sigma_2,t_2)\cdots$	Spatial, spin, and time coordinates of an electron
$\psi(r)\equiv\psi(\mathbf{r},\sigma),\quad\psi^\dagger(r)\equiv\psi^\dagger(\mathbf{r},\sigma)$	Annihilation and creation operators, respectively, of an electron at position $\mathbf{r}$ and with spin σ
$a_p,\quad a_p^\dagger$	Annihilation and creation operators, respectively, of an electron with momentum $\mathbf{p}$ and with spin σ
$\psi(r)\equiv\psi(\mathbf{r},\sigma)=\sum_{p=(\mathbf{p},m_s)}a_p\phi_p(\mathbf{r},\sigma)$	
$\psi^\dagger(r)\equiv\psi^\dagger(\mathbf{r},\sigma)=\sum_{p=(\mathbf{p},m_s)}a_p^\dagger\phi_p^*(\mathbf{r},\sigma)$	
$\phi_p(\mathbf{r},\sigma)=\phi_{\mathbf{p},m_s}(\mathbf{r},\sigma)=e^{i\mathbf{p}\cdot\mathbf{r}}\chi_{m_s}(\sigma)$	
$\psi(rt)=e^{iHt}\psi(r)e^{-iHt}$, $\psi^\dagger(rt)=e^{iHt}\psi^\dagger(r)e^{-iHt}$	Heisenberg representation of $\psi(r)$ and $\psi^\dagger(r)$, respectively
$\lvert\Psi_0\rangle$	State vector of the ground state of an atomic system of N electrons
$\lvert\Psi_m\rangle,\lvert\Psi_n\rangle,\ldots$	State vectors of the mth, nth, . . . excited states of an atomic system of N electrons
$\lvert\Psi_p^{(+)}\rangle$	Scattering state of an $(N+1)$-electron system with incident electron of quantum numbers p and target in the ground state
$\lvert\Psi_q^{(-)}\rangle$	Scattering state of an $(N+1)$-electron system with scattered electron of quantum numbers q and target in the ground state
$\lvert\Psi_{p,m}^{(+)}\rangle$	Scattering state of an $(N+1)$-electron system with incident electron of quantum numbers p and target in the Mth excited state
$\lvert\Psi_{q,n}^{(-)}\rangle$	Scattering state of an $(N+1)$-electron system with scattered electron of quantum numbers q and target in the nth excited state
$T(A(t_1)B(t_2))=\begin{cases}A(t_1)B(t_2) & \text{for } t_1>t_2\\ B(t_2)A(t_1) & \text{for } t_1<t_2\end{cases}$	T is the Wick time-ordering operator

TABLE II. Green's function, Bethe-Salpeter, and Feynman-Dyson amplitudes.

$G(1,1')=\frac{1}{i}\langle\Psi_0\lvert T[\psi(1)\psi^\dagger(1')]\rvert\Psi_0\rangle$	One-particle Green's function
$X_0^m(1,1')=\langle\Psi_0\lvert T[\psi(1)\psi^\dagger(1')]\rvert\Psi_m\rangle$	Ground-state–excited-state Bethe-Salpeter amplitude
$X_m^0(1,1')=\langle\Psi_m\lvert T[\psi(1)\psi^\dagger(1')]\rvert\Psi_0\rangle$	Excited-state–ground-state Bethe-Salpeter amplitude
$X_n^m(1,1')=\langle\Psi_n\lvert T[\psi(1)\psi^\dagger(1')]\rvert\Psi_m\rangle$	Excited-state–excited-state Bethe-Salpeter amplitude
$f_p^{(+)}(1)=\langle\Psi_0\lvert\psi(1)\rvert\Psi_p^{(+)}\rangle$	One-electron, particle-type Feynman-Dyson amplitude with outgoing-wave boundary conditions
$f_q^{(-)}(1)=\langle\Psi_0\lvert\psi(1)\rvert\Psi_q^{(-)}\rangle$	One-electron, particle-type Feynman-Dyson amplitude with incoming-wave boundary conditions
$f_p^{m(+)}(1)=\langle\Psi_m\lvert\psi(1)\rvert\Psi_p^{(+)}\rangle$	One-electron, particle-type Feynman-Dyson amplitude in reference to the mth excited state of the target with outgoing-wave boundary conditions
$f_q^{m(-)}(1)=\langle\Psi_m\lvert\psi(1)\rvert\Psi_q^{(-)}\rangle$	One-electron, particle-type Feynman-Dyson amplitude in reference to the mth excited state of the target with incoming-wave boundary conditions
$\tilde{f}_p^{m(+)}(1)=\langle\Psi_0\lvert\psi(1)\rvert\Psi_{p,m}^{(+)}\rangle$	One-electron, particle-type Feynman-Dyson amplitude associated with the $\lvert\Psi_{p,m}^{(+)}\rangle$ scattering state.
$\tilde{f}_q^{n(-)}(1)=\langle\Psi_0\lvert\psi(1)\rvert\Psi_{q,n}^{(-)}\rangle$	One-electron, particle-type Feynman-Dyson amplitude associated with the $\lvert\Psi_{q,n}^{(-)}\rangle$ scattering state.

$$a_p(t)=\int \psi(rt)\phi_p^*(rt)dr \tag{3b}$$

where $\psi(rt)=e^{iHt}\psi(r)e^{-iHt}$ is the one-electron field operator in the Heisenberg representation (see Table I). Thus the $a_p(t)$ operators are the expansion coefficients in an expansion of the $\psi(rt)$ operator in terms of the $\phi_p(rt)$ functions [see Eq. (20d) in CTY].

In order to obtain an exact formula for $S_{nq,mp}$, the limit required by Eq. (2) has to be calculated. This can be achieved most easily if an equation is obtained for the $X_n^m(1,1')$ amplitude. This can be accomplished if one starts from the time-dependent Bethe-Salpeter equation, which can be given in the form [Eq. (68) of CTY]

$$R(12,1'2^+)=G(1,2^+)G(2,1') + \int d4\,d4'd5\,d5'G(1,4)G(4',1') \times\Xi(45,4'5')R(5'2,52^+) \tag{4}$$

where

$$R(12,1'2^+)=\frac{\delta G(1,1')}{\delta U(2)} \tag{5}$$

is the linear-response function and

$$\Xi(45,4'5')=\frac{\delta\Sigma(4,4')}{\delta G(5',5)} \tag{6}$$

is the two-point vertex function. Now differentiating Eq. (4) according to the $U(3)$, an equation will be obtained for the quadratic response function $R(123,1'2^+3^+)$, defined by [see Eq. (A7) in Ref. [84]]

$$R(123,1'2^+3^+)=\frac{\delta R(12,1'2^+)}{\delta U(3)}=\frac{\delta^2 G(1,1')}{\delta U(3)\delta U(2)} \tag{7}$$

in the form

$$\begin{aligned}R(123,1'2^+3^+)=&R(13,23^+)G(2,1')+G(1,2)R(23,1'3^+)\\&+\int d4\,d4'd5\,d5'[R(13,43^+)G(4',1')+G(1,4)R(4'3,1'3^+)]\Xi(45,4'5')R(5'2,52^+)\\&+\int d4\,d4'd5\,d5'G(1,4)G(4',1')\Xi(45,4'5')R(5'23,52^+3^+)\\&+\int d4\,d4'd5\,d5'G(1,4)G(4',1')\frac{\delta\Xi(45,4'5')}{\delta U(3)}R(5'2,52^+)\,.\end{aligned} \tag{8}$$

By applying the Gell-Mann–Low [85] operator ($\mathcal{L}$) on both sides of this equation and using the identity

$$X_n^m(1,1')=\frac{1}{i}\frac{1}{d_n d_m}\mathcal{L}_{(t_2\to\infty)}\mathcal{L}_{(t_3\to-\infty)}\int dr_2 dr_3 R(123,1'2^+3^+)X_n^0(2,2^+)X_0^m(3,3^+)\,, \tag{9}$$

valid when $n\neq m$, where

$$d_m=\int dr_2 X_0^m(2,2^+)X_m^0(2,2^+)\,,$$

one obtains the following exact equation for the $X_n^m(1,1')(n\neq m)$ amplitude:

$$\begin{aligned}X_n^m(1,1')=&\frac{1}{i}\int d2\,d2'd3\,d3'[X_0^m(1,2')G(2,1')+G(1,2')X_0^m(2,1')]\Xi(2'3',23)X_n^0(3,3')\\&+\int d2\,d2'd3\,d3'G(1,2)G(2'1')\Xi(2'3'23)X_n^m(3,3')\\&+\frac{1}{i}\int d4\,d4'd5\,d5'd6\,d6'G(1,4)G(4',1')\Xi^{(3)}(456,4'5'6')X_n^0(6',6)X_0^m(5,5')\end{aligned} \tag{10}$$

where we have introduced the three-point vertex function

$$\Xi^{(3)}(456,4'5'6')=\frac{\delta\Xi(45,4'5')}{\delta G(6',6)}\,. \tag{11}$$

This equation can be used in calculating the limit required in Eq. (2). The following result is obtained then:

$$\begin{aligned}S_{nq,mp}=&-\int d2\,d2'd3\,d3'[f_q^{m(-)*}(2')f_p^{(+)}(2)+f_q^{(-)*}(2')\tilde{f}_p^{m(+)}(2)]\Xi(2'3',23)X_n^0(3,3')\\&-\int d2\,d2'd3\,d3'f_q^{(-)*}(2')f_p^{(+)}(2)\Xi(2'3',23)X_n^m(3,3')\\&-\frac{1}{i}\int d2\,d2'd3\,d3'd4\,d4'f_q^{(-)*}(2')f_p^{(+)}(2)\Xi^{(3)}(234,2'3'4')X_n^0(4,4')X_0^m(3,3')\,.\end{aligned} \tag{12}$$

(This formula is valid only for $n\neq m$.)

The Feynman-Dyson amplitudes appearing in Eq. (12) are defined in Table II. In obtaining Eq. (12) from Eqs. (2) and (10), the limiting formulas enlisted in Table III were used.

In order to calculate the S matrix given by Eq. (12), we need to know how to calculate the $\tilde{f}_p^{m(+)}$ and $f_q^{m(-)}$ functions. This can be achieved if one uses the definition of these functions (see Table II) and the equation for $X_0^m(1,1')$, which can be obtained from Eq. (4),

TABLE III. Limiting formulas for Feynman-Dyson amplitudes.

Let us introduce the notation

$$\phi_p(rt)=e^{i\mathbf{p}\cdot\mathbf{r}}\chi_{m_s}(\sigma)e^{-i\varepsilon_p t}$$

where

$$\varepsilon_p=\mathbf{p}^2/2\ ;$$

then

$$f_p^{(+)}(rt)=i\lim_{t'\to-\infty}\int dr'G(rt,r't')\phi_p(r't')$$

$$f_q^{(-)*}(rt)=i\lim_{t'\to\infty}\int dr'G(r't',rt)\phi_q^*(r't')$$

$$f_p^{m(+)}(rt)=\lim_{t'\to-\infty}\int dr'X_m^0(rt,r't')\phi_p(r't')$$

$$f_q^{m(-)*}(rt)=\lim_{t'\to\infty}\int dr'X_0^m(rt,r't')\phi_q^*(r't')$$

$$\tilde{f}_p^{m(+)}(rt)=\lim_{t'\to-\infty}\int dr'X_0^m(rt,r't')\phi_p(r't')$$

$$\tilde{f}_q^{m(-)*}(rt)=\lim_{t'\to\infty}\int dr'X_m^0(r't',rt)\phi_q^*(r't')$$

where

$$\int dr'\equiv\int d\mathbf{r}'\sum_{\sigma'}$$

refers to spatial integration and spin summation.

$$X_0^m(1,1')=\int d3\,d3'd4\,d4'G(1,3')G(3,1')\times\Xi(3'4,34)X_0^m(4,4')\ . \tag{13}$$

Then one obtains

$$\tilde{f}_p^{m(+)}(1)=\frac{1}{i}\int d3\,d3'd4\,d4'G(1,3')f_p^{(+)}(3)\times\Xi(3'4',34)X_0^m(4,4')\ . \tag{14}$$

The appropriate equation for $f_q^{m(-)*}(1)$ can also be obtained from Eq. (13) using the definition in Table II, providing

$$f_q^{m(-)*}(1')=\frac{1}{i}\int d3\,d3'd4\,d4'f_q^{(-)*}(3')G(3,1')\times\Xi(3'4',34)X_0^m(4,4')\ . \tag{15}$$

This completes the general considerations with respect to the exact S-matrix formula.

B. First-order approximation

The first-order approximation will be defined by the following equations [86]:

$$\Xi(3'4',34)=-i\delta(3-3')\delta(4-4')V(3-4)+i\delta(3'-4)\delta(3-4')V(3-3')\equiv\tilde{V}(3'4',34) \tag{16}$$

where (using hartree atomic units)

$$V(1-2)\equiv\delta(t_1-t_2)V(\mathbf{r}_1-\mathbf{r}_2)=\delta(t_1-t_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \tag{17}$$

and

$$G(1,1')=G_{\mathrm{HF}}(1,1') \tag{18}$$

where G_{HF} is the Hartree-Fock (HF) Green's function and

$$X_0^m(1,1')=X_0^{m,\mathrm{RPA}}(1,1')\ , \tag{19a}$$

$$X_m^0(1,1')=X_m^{0,\mathrm{RPA}}(1,1') \tag{19b}$$

where $X_0^{m,\mathrm{RPA}}$ ($X_m^{0,\mathrm{RPA}}$) refers to the X_0^m (X_m^0) amplitude in the random-phase approximation (RPA). $X_0^{m,\mathrm{RPA}}$ satisfies Eq. (13) if the $G=G_{\mathrm{HF}}$ and $\Xi\equiv\tilde{V}$ approximations are used in it. (For the definition of the Hartree-Fock Green's function see, e.g., CTY.)

From Eqs. (11) and (16) it immediately follows that in our first-order scheme

$$\Xi^{(3)}(456,4'5'6')\equiv0\ . \tag{20}$$

The first-order formula for the S matrix is obtained if the

$$\Xi\equiv\tilde{V}\ ,\quad \Xi^{(3)}\equiv0$$

substitutions are made in Eq. (11) as well as in Eqs. (14) and (15) in obtaining the $\tilde{f}_p^{m(+)}(1)$ and $f_q^{m(-)}(1)$ functions. Besides, in Eq. (12) we substitute $f_p^{(+)}=f_p^{(+)\mathrm{HF}}$ and $f_q^{(-)}\equiv f_q^{(-)\mathrm{HF}}$ where $f_p^{(+)\mathrm{HF}}$ and $f_q^{(-)\mathrm{HF}}$ are the Hartree-Fock approximations for the Feynman-Dyson amplitudes (they are also called static-exchange orbitals) and in Eq. (14) and (15) we use the $G=G_{\mathrm{HF}}$, $\Xi=\tilde{V}$, $f_p^{(+)}=f_p^{(+)\mathrm{HF}}$, and $f_q^{(-)}=f_q^{(-)\mathrm{HF}}$ substitutions. [See Eq. (16).]

In order to get our working formulas we need to change from time to energy variables, i.e., to effect a Fourier transformation. This can be facilitated if the following factorizations are introduced (see, e.g., CTY):

$$X_0^m(1,1')=\exp\left[-\omega_m\frac{(t_1+t_1')}{2}\right]X_0^m(r_1r_1';\tau_1) \tag{21a}$$

where

$$\tau_1=t_1-t_1' \tag{21b}$$

and $\omega_m=E_m-E_0$ is the excitation energy of the mth excited state,

$$f_p^{(+)}(1)=e^{-i\varepsilon_p t_1}f_p(r_1)\ , \tag{21c}$$

$$f_q^{(-)*}(1)=e^{i\varepsilon_q t_1}f_q^{(-)*}(r_1) \tag{21d}$$

where ε_p and ε_q are the kinetic energies of the incident and scattered electrons, respectively, and

$$\tilde{f}_p^{m(+)}(1)=e^{-i(\omega_m+\varepsilon_p)t_1}\tilde{f}_p^{m(+)}(r_1)\ , \tag{21e}$$

$$f_q^{m(-)*}(1)=e^{-i(\omega_m-\varepsilon_q)t_1}f_q^{m(-)*}(r_1)\ . \tag{21f}$$

If these factorizations are used in the first-order S-matrix

formula as well as in the first-order equations for the $\tilde{f}_p^{m(+)}(1)$ and $f_q^{m(-)*}(1)$ amplitudes, and the notation introduced

$$W(r_1'r_2',r_1r_2)=[\delta(r_1-r_1')\delta(r_2-r_2') -\delta(r_1'-r_2')\delta(r_1-r_2)]V(\mathbf{r}_1-\mathbf{r}_2) \quad (22)$$

where

$$\delta(r_1-r_2)=\delta(\mathbf{r}_1-\mathbf{r}_2)\delta_{\sigma_1\sigma_2} ,$$
$$V(\mathbf{r}_1-\mathbf{r}_2)=1/|\mathbf{r}_1-\mathbf{r}_2| ,$$

then the following formulas are obtained:

$$[\omega_m+\varepsilon_p-h(r')]\tilde{f}_p^{m(+)}(r')-\int dr\,\Sigma_{\mathrm{HF}}(r',r)\tilde{f}_p^{m(+)}(r) =\int dr_1dr_2dr_2'f_p^{(+)}(r_1)W(r'r_2',r_1r_2)X_m(r_2'r_2) , \quad (23a)$$

$$[\varepsilon_q-\omega_m-h(r)]f_q^{m(-)*}(r)-\int dr'\Sigma_{\mathrm{HF}}(r',r)f_q^{m(-)*}(r') =\int dr_1'dr_2dr_2dr_2'f_q^{(-)*}(r_1')W(r_1'r_2',rr_2)X_m(r_2'r_2) , \quad (23b)$$

and

$$S_{nq,mp}^{\mathrm{FOMBT}}=-2\pi i\left\{\int dr_1dr_1'dr_2dr_2'[f_q^{m(-)*}(r_1')f_p^{(+)\mathrm{HF}}(r_1)+f_q^{(-)\mathrm{HF}*}(r_1')\tilde{f}_p^{m(+)}(r_1)]W(r_1'r_2',r_1r_2)\tilde{X}_n(r_2'r_2) + \int dr\,dr_1'dr_2dr_2'f_q^{(-)\mathrm{HF}*}(r_1')f_p^{\mathrm{HF}(+)}(r_1')W(r_1'r_2',r_1r_2)X_n^m(r_2'r_2)\right\} . \quad (24)$$

This is our first-order formula and valid for $n\neq m$. Equations (23a) and (23b) describe coupled channels in which the initial state m is coupled to the ground state and to a doubly excited state, respectively.

In the above formulas, the various terms can be represented by Feynman-like diagrams as shown in Fig. 2. The interpretation of the various terms in Eq. (24) in terms of a coupled channel scheme is shown in Fig. 3. The quantities

$$X_n(rr')=\langle\Psi_0|\psi^\dagger(r)\psi(r')|\Psi_n\rangle , \quad (25a)$$
$$\tilde{X}_n(rr')=\langle\Psi_n|\psi^\dagger(r)\psi(r')|\Psi_0\rangle , \quad (25b)$$
$$X_n^m(rr')=\langle\Psi_n|\psi^\dagger(r)\psi(r')|\Psi_m\rangle \quad (25c)$$

are transition density matrices, and $h(r)=-\frac{1}{2}\nabla^2-Z/|\mathbf{r}|$, where Z is the nuclear charge and Σ_{HF} is the Hartree-Fock potential.

C. Spin factorization

In the following we shall write

$$m=\bar{m}L^mM_L^mS^mM_S^m$$

and

$$n=\bar{n}L^nM_L^nS^nM_S^n$$

where $L^mM_L^mS^mM_S^m$ ($L^nM_L^nS^nM_S^n$) refer to the angular momentum and spin quantum numbers of state m (n), and $\bar{m}$ ($\bar{n}$) refer to all other quantum numbers. It can be shown easily that the $X_m(r'r)$ amplitude can be written in the following spin-factorized form:

$$X_m(r'r)=X_m(\mathbf{r}'\mathbf{r})\xi_{S^mM_S^m}(\sigma'\sigma) \quad (26)$$

[the subindex of the $X_m(\mathbf{r}'\mathbf{r})$ amplitude could have been written as $\bar{m},S^m$] where the two-electron spin function ξ_{S^m,M_S^m} is defined by the formula

$$\xi_{S^m,M_S^m}(\sigma'\sigma) =\sum_{m_1,m_2}(-1)^{1/2+m_1}C^{1/2\ 1/2\ S_m}_{-m_1\ m_2\ M_S^m}\eta_{m_1}^{*(\sigma')}\eta_{m_2}^{(\sigma)} \quad (27)$$

with $C^{j_1j_2j_3}_{m_1m_2m_3}$ referring to the Clebsch-Gordan coefficient and $\eta_{m_S}(\sigma)$ to the Pauli spin function. We can assume

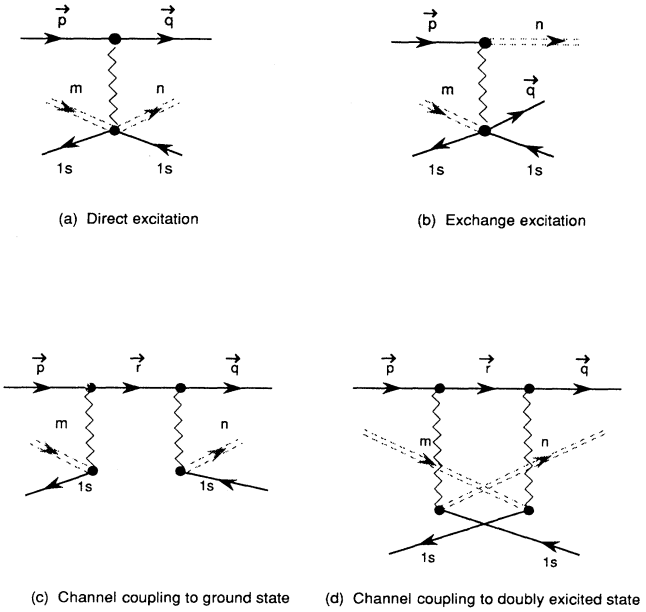

FIG. 2. Feynman-type diagram for the illustration of direct (exchange) excitation terms included into the FOMBT of electron-impact excitation out of excited states. The He atom is used here as an example. The solid lines with arrows to the right refer to $e+$He scattering (continuum) orbitals; the double solid lines (with arrows to the right) refer to excited (bound or continuum) state orbitals of the He atom. Solid lines with arrows to the left refer to the (ground state) $1s$ orbital of He.

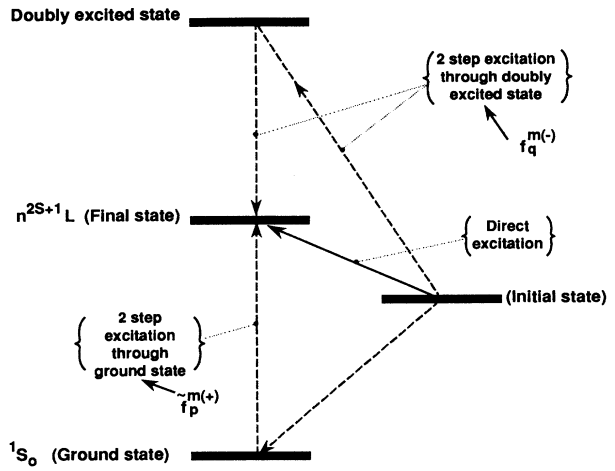

FIG. 3. Schematic representation, in terms of coupled channels, of the physical processes included in the FOMBT of electron-impact excitation out of excited states. [See Eqs. (23a) and (23b) and (24) and comments following.]

the following spin factorizations of the Hartree-Fock scattering orbital and Hartree-Fock Green's function, respectively:

$$f_p^{(+)\mathrm{HF}}(r)=f_{\mathbf{p}}^{(+)\mathrm{HF}}(\mathbf{r})\eta_{m_{s_p}}(\sigma) \tag{28}$$

and

$$G_{\mathrm{HF}}(r,r';\varepsilon)=G_{\mathrm{HF}}(\mathbf{r},\mathbf{r}';\varepsilon)\delta_{\sigma\sigma'} . \tag{29}$$

Using Eqs. (26), (28), and (29) in the integral form of Eq. (23a), we obtain the spin-factorized form of $\tilde{f}_p^{m(+)}(r)$ as

$$\tilde{f}_p^{m(+)}(r)=(-1)^{1/2+m_{S_p}}C^{1/2\ 1/2\ S^m}_{-m_{S_p}\ m_S\ M_S^m}\tilde{f}_{\mathbf{p}}^{m(+)}(\mathbf{r})\eta_{m_s}(\sigma) \tag{30}$$

where evidently $m_s=m_{s_p}+M_S^m$ and the spatial part $\tilde{f}_{\mathbf{p}}^{m(+)}(\mathbf{r})$ has the form

$$\tilde{f}_{\mathbf{p}}^{m(+)}(\mathbf{r})=2\tilde{f}_{\mathbf{p},1}^{m(+)}(\mathbf{r})\delta_{S^m,0}-\tilde{f}_{\mathbf{p},2}^{m(+)}(\mathbf{r}) \tag{31}$$

where $\tilde{f}_{\mathbf{p},1}^{(+)m}(\mathbf{r})$ and $\tilde{f}_{\mathbf{p},2}^{(+)m}(\mathbf{r})$ are given by the following equations:

$$\tilde{f}_{\mathbf{p},1}^{m(+)}(\mathbf{r})=\int d\mathbf{r}_1 d\mathbf{r}_2 G_{\mathrm{HF}}(\mathbf{r},\mathbf{r}_1;\varepsilon_p+\omega_m)f_{\mathbf{p}}^{(+)\mathrm{HF}}(\mathbf{r}_1)\times V(\mathbf{r}_1-\mathbf{r}_2)X_m(\mathbf{r}_2\mathbf{r}_2) , \tag{32a}$$

$$\tilde{f}_{\mathbf{p},2}^{m(+)}(\mathbf{r})=\int d\mathbf{r}_1 d\mathbf{r}_2 G_{\mathrm{HF}}(\mathbf{r},\mathbf{r}_2;\varepsilon_p+\omega_m)f_{\mathbf{p}}^{(+)\mathrm{HF}}(\mathbf{r}_1)\times V(\mathbf{r}_1-\mathbf{r}_2)X_m(\mathbf{r}_1,\mathbf{r}_2) . \tag{32b}$$

Thus we obtain for $\tilde{f}_{\mathbf{p}}^{m(+)}(\mathbf{r})$,

$$[\varepsilon_p+\omega_m-h(\mathbf{r})]\tilde{f}_{\mathbf{p}}^{m(+)}(\mathbf{r})-\int d\mathbf{r}_1\,\Sigma_{\mathrm{HF}}(\mathbf{r},\mathbf{r}_1)\tilde{f}_{\mathbf{p}}^{m(+)}(\mathbf{r}_1)=2\delta_{S^m,0}f_{\mathbf{p}}^{\mathrm{HF}(+)}(\mathbf{r})\int d\mathbf{r}_1 V(\mathbf{r}-\mathbf{r}_1)X_m(\mathbf{r}_1\mathbf{r}_1)-\int d\mathbf{r}_1 f_{\mathbf{p}}^{\mathrm{HF}(+)}(\mathbf{r}_1)V(\mathbf{r}-\mathbf{r}_1)X_m(\mathbf{r}_1\mathbf{r}) . \tag{33}$$

Assuming the factorization

$$f_q^{(-)\mathrm{HF}}(r)=f_{\mathbf{q}}^{(-)\mathrm{HF}}(\mathbf{r})\eta_{m_{s_q}}(\sigma) \tag{34}$$

for the outgoing-wave continuum orbital we obtain from the integral form of Eq. (23b) the spin factorization of $f_q^{m(-)}(r)$ in the form

$$f_q^{m(-)}(r)=(-1)^{1/2+m_S}C^{1/2\ 1/2\ S^m}_{-m_S\ m_{S_q}\ M_S^m}f_{\mathbf{q}}^{m(-)}(\mathbf{r})\eta_{m_s}(\sigma) \tag{35}$$

where $m_s=m_{s_q}-M_S^m$ and $f_{\mathbf{q}}^{m(-)}(\mathbf{r})$ is given as

$$f_{\mathbf{q}}^{m(-)}(\mathbf{r})=2\delta_{S^m,0}f_{\mathbf{q},1}^{m(-)}(\mathbf{r})-f_{\mathbf{q},2}^{m(-)}(\mathbf{r}) \tag{36}$$

with $f_{\mathbf{q},1}^{m(-)}(\mathbf{r})$ and $f_{\mathbf{q},2}^{m(-)}(\mathbf{r})$ defined by the equations

$$f_{\mathbf{q},1}^{m(-)*}(\mathbf{r})=\int d\mathbf{r}_1 d\mathbf{r}_2 f_{\mathbf{q}}^{(-)\mathrm{HF}*}(\mathbf{r}_1)G_{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r};\varepsilon_q-\omega_m)V(\mathbf{r}_1-\mathbf{r}_2)X_m(\mathbf{r}_2\mathbf{r}_2) , \tag{37a}$$

$$f_{\mathbf{q},2}^{m(-)*}(\mathbf{r})=\int d\mathbf{r}_1 d\mathbf{r}_2 f_{\mathbf{q}}^{(-)\mathrm{HF}*}(r_2)G_{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r};\varepsilon_q-\omega_m)V(\mathbf{r}_1-\mathbf{r}_2)X_m(\mathbf{r}_1\mathbf{r}_2) , \tag{37b}$$

and we obtain the following equation for the $f_{\mathbf{q}}^{m(-)*}(\mathbf{r})$ function:

$$[\varepsilon_q-\omega_m-h(\mathbf{r})]f_{\mathbf{q}}^{m(-)*}(\mathbf{r})-\int d\mathbf{r}_1\Sigma_{\mathrm{HF}}(\mathbf{r},\mathbf{r}_1)f_{\mathbf{q}}^{m(-)*}(\mathbf{r}_1)=2\delta_{S^m,0}f_{\mathbf{q}}^{(-)\mathrm{HF}*}(\mathbf{r})\int d\mathbf{r}_2 V(\mathbf{r}-\mathbf{r}_2)X_m(\mathbf{r}_2\mathbf{r}_2)-\int d\mathbf{r}_1 f_{\mathbf{q}}^{(-)*}(\mathbf{r}_1)V(\mathbf{r}-\mathbf{r}_1)X_m(\mathbf{r}\mathbf{r}_1) . \tag{38}$$

In order to complete our spin analysis we need to execute the spin summations in the electron scattering T matrix. For that reason we need to discuss here also the spin factorization of the X_n and $\tilde{X}_n$ amplitudes. From the definitions of X_n and $\tilde{X}_n$ it immediately follows that

$$\tilde{X}_m(rr')=X_m^*(r'r) , \tag{39}$$

which yields the factorization of $\tilde{X}_n$, which will be written here in the form

$$\tilde{X}_n(rr')=(-1)^{S^n-M_S^n}\tilde{X}_n(\mathbf{r}\mathbf{r}')\xi_{S^n,-M_S^n}(\sigma\sigma') \tag{40}$$

where

$$\tilde{X}_n(\mathbf{r}\mathbf{r}')=(-1)^{S^n}X_n^*(\mathbf{r}'\mathbf{r}) . \tag{41}$$

The spin analysis of the X_n^m amplitude is somewhat more involved because both n and m can refer to triplet states. Using tensor algebra along with the Wigner-Eckart theorem it can be shown that X_n^m can be spin analyzed in the form

$$X_n^m(rr')=\sum_{k,q}(-1)^{k-q}C^{k\ S^m\ S^n}_{q\ M_S^m\ M_S^n}\xi_{k,-q}(\sigma,\sigma')X_n^{m(k)}(\mathbf{r}\mathbf{r}') . \tag{42}$$

Subsequently we shall discuss the form of $X_n^{m(k)}(\mathbf{r}\mathbf{r}')$ in our approximation. Now the above spin factorizations can be introduced into the various terms of our T matrix and the spin summations executed providing the following expressions, term by term:

$$T^{\mathrm{I}}_{nq,mp}\equiv\int dr\,dr' f_q^{m(-)*}(r)f_p^{(+)\mathrm{HF}}(r)V(\mathbf{r}-\mathbf{r}')\tilde{X}_n(r'r')$$
$$=(-1)^{1/2+m_{S_p}}C^{1/2\ 1/2\ S^m}_{-m_{s_p}\ m_s\ M_S^m}\sqrt{2}\delta_{S^n,0}I_1 \tag{43}$$

where

$$I_1=\int d\mathbf{r}\,d\mathbf{r}' f_{\mathrm{q}}^{m(-)*}(\mathbf{r})f_{\mathrm{p}}^{(+)\mathrm{HF}}(\mathbf{r})V(\mathbf{r}-\mathbf{r}')\tilde{X}_n(\mathbf{r}'\mathbf{r}') , \tag{44}$$

$$T^{\mathrm{II}}_{nq,mp}\equiv\int dr\,dr' f_q^{(-)\mathrm{HF}*}(r)\tilde{f}_p^{m(+)}(r)V(\mathbf{r}-\mathbf{r}')\tilde{X}_n(r'r')$$
$$=(-1)^{1/2+m_{S_p}}C^{1/2\ 1/2\ S^m}_{-m_{s_p}\ m_s\ M_S^m}\sqrt{2}\delta_{S^n,0}I_2 ; \tag{43'}$$

where

$$I_2=\int d\mathbf{r}\,d\mathbf{r}' f_{\mathrm{q}}^{(-)\mathrm{HF}*}(\mathbf{r})\tilde{f}_{\mathrm{p}}^{m(+)}(\mathbf{r})V(\mathbf{r}-\mathbf{r}')\tilde{X}_n(\mathbf{r}'\mathbf{r}') , \tag{44'}$$

$$T^{\mathrm{III}}_{nq,mp}\equiv\int dr\,dr' f_q^{m(-)*}(r')f_p^{(+)\mathrm{HF}}(r)$$
$$\times V(\mathbf{r}-\mathbf{r}')\tilde{X}_n(rr')$$
$$=(-1)^{S^m}C^{1/2\ 1/2\ S^m}_{-m_s\ m_{s_q}\ M_S^m}C^{1/2\ 1/2\ S^n}_{-m_{s_p}\ m_s\ -M_S^n}I_3 ; \tag{43''}$$

where

$$I_3=\int d\mathbf{r}\,d\mathbf{r}' f_{\mathrm{q}}^{m(-)*}(\mathbf{r}')f_{\mathrm{p}}^{(+)\mathrm{HF}}(\mathbf{r})V(\mathbf{r}-\mathbf{r}')\tilde{X}_n(\mathbf{r}\mathbf{r}') , \tag{44''}$$

$$T^{\mathrm{IV}}_{nq,mp}\equiv\int dr\,dr' f_q^{(-)\mathrm{HF}*}(r')\tilde{f}_p^{m(+)}(r)$$
$$\times V(\mathbf{r}-\mathbf{r}')\tilde{X}_n(rr')$$
$$=(-1)^{S^n+M_S^m-M_S^n}C^{1/2\ 1/2\ S^m}_{-m_{s_p}\ m_s\ m_S^m}C^{1/2\ 1/2\ S^n}_{-m_s\ m_{s_q}\ -M_S^n}I_4 ; \tag{43'''}$$

where

$$I_4=\int d\mathbf{r}\,d\mathbf{r}' f_{\mathrm{q}}^{(-)\mathrm{HF}*}(\mathbf{r}')\tilde{f}_{\mathrm{p}}^{m(+)}(\mathbf{r})V(\mathbf{r}-\mathbf{r}')\tilde{X}_n(\mathbf{r}\mathbf{r}') , \tag{44'''}$$

$$T^{\mathrm{V}}_{nq,mp}\equiv\int dr\,dr' f_q^{(-)\mathrm{HF}*}(r)f_p^{(+)\mathrm{HF}}(r)$$
$$\times V(\mathbf{r}-\mathbf{r}')\tilde{X}_n^m(r'r')$$
$$=\delta_{m_{s_p},m_{s_q}}\delta_{S^m,S^n}\delta_{M_S^m,M_S^n}\sqrt{2}I_5 ; \tag{43''''}$$

where

$$I_5=\int d\mathbf{r}\,d\mathbf{r}' f_{\mathrm{q}}^{(-)\mathrm{HF}*}(\mathbf{r})f_{\mathrm{p}}^{(+)\mathrm{HF}}(\mathbf{r})$$
$$\times V(\mathbf{r}-\mathbf{r}')\tilde{X}_n^{m(0)}(\mathbf{r}'\mathbf{r}') , \tag{44''''}$$

$$T^{\mathrm{VI}}_{nq,mp}\equiv\int dr\,dr' f_q^{(-)\mathrm{HF}*}(r')f_p^{(+)\mathrm{HF}}(r)$$
$$\times V(\mathbf{r}-\mathbf{r}')\tilde{X}_n^m(rr')$$
$$=\sum_{k,q}(-1)^{k-q}C^{k\ S^m\ S^n}_{q\ M_S^m\ M_S^n}(-1)^{1/2+m_{S_p}}$$
$$\times C^{1/2\ 1/2\ S^m}_{-m_{s_p}\ m_{s_q}\ -q}I_6^{(k)} ; \tag{43'''''}$$

and where

$$I_6^{(k)}=\int d\mathbf{r}\,d\mathbf{r}' f_{\mathrm{q}}^{(-)\mathrm{HF}*}(\mathbf{r}')f_{\mathrm{p}}^{(+)\mathrm{HF}}(\mathbf{r})$$
$$\times V(\mathbf{r}-\mathbf{r}')X_n^{m(k)}(\mathbf{r}\mathbf{r}') . \tag{44'''''}$$

D. Angular momentum analysis

In order to implement our scheme numerically, we need to reduce partial integro-differential equations to coupled conventional integro-differential equations. This is most conveniently accomplished by performing an angular momentum analysis. The continuum Hartree-Fock orbitals will be expanded in the form

$$f_{\mathrm{p}}^{(\pm)}(\mathbf{r})=\sqrt{8/p}\,\pi^{3/2}\sum_{l,m}i^l e^{\pm i\delta_l(p)}\frac{P_{p,l}(r)}{r}$$
$$\times Y_{lm}(\hat{\mathbf{r}})Y_{lm}^*(\hat{\mathbf{p}}) , \tag{45}$$

where r (p) and $\hat{\mathbf{r}}$ ($\hat{\mathbf{p}}$) refer to the radial and angular coordinates of $\mathbf{r}$ ($\mathbf{p}$), respectively, $Y_{lm}(\hat{\mathbf{r}})$ is the usual spherical harmonic and the radial functions $P_{p,l}(r)$ have the asymptotic form

$$P_{p,l}(r)\underset{r\to\infty}{\sim}\sqrt{2/\pi p}\sin\left[pr-\frac{l\pi}{2}+\delta_l(p)\right] \tag{46}$$

where $\delta_l(p)$ is the phase shift of the lth partial wave for incident momentum p. Analogous partial wave expansions can be introduced for the Hartree-Fock Green's function $G_{\mathrm{HF}}(\mathbf{r},\mathbf{r}';\varepsilon)$, and potential $\Sigma_{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$, respectively, in the form

$$G_{\mathrm{HF}}(\mathbf{r},\mathbf{r}';\varepsilon)=\sum_{l,m}\frac{G_l^{\mathrm{HF}}(r,r';\varepsilon)}{rr'}Y_{lm}(\hat{\mathbf{r}})Y_{lm}^*(\hat{\mathbf{r}}') , \tag{47}$$

$$\Sigma_{\mathrm{HF}}(\mathbf{r},\mathbf{r}')=\sum_{l,m}\frac{\Sigma_l^{\mathrm{HF}}(r,r')}{rr'}Y_{lm}(\hat{\mathbf{r}})Y_{lm}^*(\hat{\mathbf{r}}') . \tag{48}$$

(For the rest of this section, r will always refer to the

magnitude of the $\mathbf{r}$ vector.) From

$$h(\mathbf{r})G_{\mathrm{HF}}(\mathbf{r},\mathbf{r}';\varepsilon)-\int d\mathbf{r}''\Sigma_{\mathrm{HF}}(\mathbf{r},\mathbf{r}'')G_{\mathrm{HF}}(\mathbf{r}'',\mathbf{r}';\varepsilon) -\varepsilon G_{\mathrm{HF}}(\mathbf{r},\mathbf{r}';\varepsilon)=\delta(\mathbf{r}-\mathbf{r}') \quad (49)$$

it follows that

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-\varepsilon\right]G_l^{\mathrm{HF}}(r,r';\varepsilon) -\int dr''\Sigma_l^{\mathrm{HF}}(r,r'')G_l^{\mathrm{HF}}(r'',r';\varepsilon)=\delta(r-r') \ . \quad (50)$$

In Eq. (49) $h(\mathbf{r})=-\frac{1}{2}\nabla^2-Z/r$ where Z is the nuclear charge.

The angular momentum expansions introduced above allow us now to introduce analogous expansions for the $\tilde{f}_{\mathbf{p}}^{m(+)}(\mathbf{r})$ and $f_{\mathbf{q}}^{m(-)}(\mathbf{r})$ functions. These expansions take a fairly complicated form in the most general case and here we shall restrict ourselves to situations where $L^m=0$; i.e., the initial excited state is an S state. (In the following all formulas will be relevant to only this case. Our primary interest is to consider electron-impact excitation out of the $2\,^3S$ and $2\,^1S$ states of He.) In this special case the following expansions can be assumed for $\tilde{f}_{\mathbf{p}}^{m(+)}(\mathbf{r})$ and $f_{\mathbf{q}}^{m(-)}(\mathbf{r})$,

$$\tilde{f}_{\mathbf{p}}^{m(+)}(\mathbf{r})=\sqrt{8/p}\,\frac{\pi^{3/2}}{r}\sum_{l,m} i^l\frac{e^{i\delta_l(p)}}{(2l+1)^{1/2}} \times F_{p,l}(r)Y_{lm}(\hat{\mathbf{r}})Y_{lm}^*(\hat{\mathbf{p}}) \ , \quad (51)$$

$$f_{\mathbf{q}}^{m(-)}(\mathbf{r})=\sqrt{8/q}\,\frac{\pi^{3/2}}{r}\sum_{l,m} i^l\frac{e^{-i\delta_l(q)}}{(2l+1)^{1/2}} \times G_{q,l}(r)Y_{lm}(\hat{\mathbf{r}})Y_{lm}^*(\hat{\mathbf{q}}) \ . \quad (52)$$

We also need the angular momentum factorization of $X_m(\mathbf{r}'\mathbf{r})$, $\tilde{X}_m(\mathbf{r}'\mathbf{r})$, and $X_n^{m(k)}(\mathbf{r}\mathbf{r}')$ amplitudes. It can be shown easily that in the case of a ^1S ground state (which is assumed in our case) one can factorize $X_m(\mathbf{r}'\mathbf{r}')$ in the form

$$X_m(\mathbf{r}\mathbf{r}')=X_m(rr')Y_{L^mM_L^m}(\hat{\mathbf{r}})Y_{00}(\hat{\mathbf{r}}') \ . \quad (53)$$

The factorization of $\tilde{X}_m(\mathbf{r}\mathbf{r}')$ follows immediately from Eqs. (41) and (53). The angular momentum factorization of $X_n^{m(k)}(\mathbf{r}\mathbf{r}')$ is quite complicated in general; however, in the present case, where it is assumed that $L_m=0$, the factorization of $X_n^{m(k)}(\mathbf{r}\mathbf{r}')$ also takes the simple form of Eq. (53),

$$X_n^{m(k)}(\mathbf{r}\mathbf{r}')=X_n^{m(k)}(rr')Y_{L^nM_L^n}(\hat{\mathbf{r}})Y_{00}(\hat{\mathbf{r}}') \ . \quad (54)$$

Using now the above angular factorizations, Eqs. (23a), and (23b) can be reduced to conventional integro-differential equations, and the S-matrix element, given by Eq. (24), can be reduced to one-dimensional repeated integrals.

Here we shall give only the integro-differential equations for the $F_{p,l}(r)$ and $G_{q,l}(r)$ functions that take the form

$$\left\{\frac{d^2}{dr^2}+2(\varepsilon_p+\omega_m)+\frac{2Z}{r}-\frac{l(l+1)}{r^2}\right\}F_{p,l}(r)-2\int dr'\Sigma_l^{\mathrm{HF}}(r,r')F_{p,l}(r') =4\delta_{S^M,0}P_{p,l}(r)(2l+1)^{1/2}\int dr'\frac{1}{r_>}X_m(r'r')-2\frac{1}{(2l+1)^{1/2}}\int dr'\frac{r_<^l}{r_>^{l+1}}X_m(rr')P_{p,l}(r') \ , \quad (55)$$

$$\left\{\frac{d^2}{dr^2}+2(\varepsilon_q-\omega_m)+\frac{2Z}{r}-\frac{l(l+1)}{r^2}\right\}G_{q,l}(r)-2\int dr'\Sigma_l^{\mathrm{HF}}(r,r')G_{q,l}(r') =4\delta_{S^M,0}(2l+1)^{1/2}\int dr'\frac{1}{r_>}X_m(r'r')-2\frac{1}{(2l+1)^{1/2}}\int dr'\frac{r_<^l}{r_>^{l+1}}X_m(rr')P_{q,l}(r') \quad (56)$$

where we used the notation $r_<=\min(r,r')$ and $r_>=\max(r,r')$.

E. Cross-section formulas

In a conventional electron-scattering experiment, unpolarized electrons are scattered from a target whose spatial and spin orientation is random. Thus the cross section measured includes an averaging over these unknown quantum numbers as well as a sum over the spin and orientation quantum numbers of the final state. If we use the notation introduced in Sec. II D, then the measured differential cross section can be given as

$$\frac{d\sigma}{d\Omega}=\frac{1}{4\pi^2}\frac{q}{p}\frac{1}{2}\frac{1}{2S^m+1}\sum_{m_{s_p}}\sum_{M_S^m}\sum_{m_{s_q}}\sum_{M_S^n}|T_{nq,mp}|^2 \ . \quad (57)$$

Here we shall collect the cross-section formulas for the various spin arrangements using our first-order theory for the T matrix.

$S^m=0,S^n=0$: singlet-singlet transition

$$\frac{d\sigma}{d\Omega}=\frac{1}{4\pi^2}\frac{q}{p}\left|I_1+I_2-\frac{1}{2}(I_3+I_4)+\sqrt{2}I_5-\frac{1}{\sqrt{2}}I_6^{(0)}\right|^2 \ . \quad (58a)$$

$S^m=1,S^n=0$: triplet-singlet transition

$$\frac{d\sigma}{d\Omega}=\frac{1}{8\pi^2}\frac{q}{p}\left|\sqrt{2}(I_1+I_2)-\frac{1}{\sqrt{2}}(I_3+I_4)-\frac{1}{\sqrt{3}}I_6^{(1)}\right|^2 \ . \quad (58b)$$

$S^m=0, S^n=1$: singlet-triplet transition

$$\frac{d\sigma}{d\Omega}=\frac{3}{8\pi^3}\frac{q}{p}\left|\frac{1}{\sqrt{2}}(I_3+I_4)+I_6^{(1)}\right|^2 . \tag{58c}$$

$S^m=1, S^n=1$: triplet-triplet transition

$$\begin{aligned}\frac{d\sigma}{d\Omega}=&\frac{1}{12\pi^2}\frac{q}{p}\left|I_3+\sqrt{2}I_5-\frac{1}{\sqrt{2}}I_6^{(0)}+\frac{1}{2}+I_6^{(1)}\right|^2\\&+\left|I_4+\sqrt{2}I_5-\frac{1}{\sqrt{2}}I_6^{(0)}-\frac{1}{2}I_6^{(1)}\right|^2\\&+|I_3-I_4+I_6^{(1)}|^2\\&+\left|\frac{1}{2}(I_3+I_4)+\sqrt{2}I_5-\frac{1}{\sqrt{2}}I_6^{(0)}\right|^2 .\end{aligned} \tag{58d}$$

In the above formulas $d\sigma/d\Omega$ refers to the differential cross section and the integrals I_n $(n=1,2,\ldots,5), I_6^{(k)}$ were defined in Sec. II C.

III. REFORMULATION OF THE GENERAL MANY-BODY THEORY OF ELECTRON-IMPACT EXCITATION OF EXCITED ATOMIC SYSTEMS

In order to get a better physical insight into the general theory of many-body Green's function for electron-impact excitation of excited atomic systems we shall reformulate the general formalism presented in Secs. I and II much along the same lines as done earlier by Csanak, Taylor, and Tripathy for excitations out of the ground state [81]. This latter work will be referred to in the future as CTT.

Our starting point will be the equation connecting the generalized linear-response function, defined by the formula [Eq. (5)],

$$R(12,1'2^+)=\frac{\delta G(1,1')}{\delta U(2)} , \tag{59}$$

to the functional derivative of the optical potential $\delta\Sigma/\delta U$, and which can be given in the form

$$\begin{aligned}R(12,1'2^+)=&G(1,2)G(2,1')\\&+\int d4\,d4'G(1,4)G(4',1')\frac{\delta\Sigma(4,4')}{\delta U(2)} .\end{aligned} \tag{60}$$

[This equation can be obtained from Eq. (4) by using the "chain rule" backwards.] From Eq. (60) it follows then that the quadratic response function defined by the formula [Eq. (7)],

$$R(123,1'2^+3^+)=\frac{\delta^2 G(1,1')}{\delta U(3)\delta U(2)} , \tag{61}$$

satisfies the following equation:

$$\begin{aligned}R(123,1'2^+3^+)=&R(13,23^+)G(2,1')+G(1,2)R(23,1'3^+)\\&+\int d4\,d4'[R(13,43^+)G(4',1')+G(1,4')R(4'3,1'3^+)]\frac{\delta\Sigma(4,4')}{\delta U(2)}\\&+\int d4\,d4'G(1,4)G(4',1')\frac{\delta^2\Sigma(4,4')}{\delta U(2)\delta U(3)} .\end{aligned} \tag{62}$$

If we use now the identity [Eq. (9)]

$$\begin{aligned}X_n^m(1,1')=&\frac{1}{i}\frac{1}{d_n d_m}\mathcal{L}_{(t_2\to\infty)}\mathcal{L}_{(t_3\to-\infty)}\\&\times\int dr_2 dr_3 R(123,1'2^+3^+)X_n^0(2,2^+)\\&\times X_0^m(3,3^+) ,\end{aligned} \tag{63}$$

where $\mathcal{L}$ refers to the Gell-Mann–Low operator [85], then we obtain from Eq. (62)

$$\begin{aligned}X_n^m(1,1')=&\int d4\,d4'[X_0^m(1,4)G(4',1')\\&+G(1,4)X_0^m(4',1')]V_{0n}(4,4')\\&+\int d4\,d4'G(1,4)G(4',1')V_{mn}(4,4') ,\end{aligned} \tag{64}$$

where we have introduced the V_{0n} and V_{mn} optical coupling potentials (or transition potentials) by the definitions, respectively,

$$V_{0n}(1,1')=\frac{1}{i}\frac{1}{d_n}\mathcal{L}_{(t_2\to\infty)}\int dr_2\frac{\delta\Sigma(1,1')}{\delta U(2)}X_n^0(2,2^+) \tag{65}$$

and

$$\begin{aligned}V_{mn}(1,1')=&\frac{1}{i}\frac{1}{d_n d_m}\mathcal{L}_{(t_2\to\infty)}\mathcal{L}_{(t_3\to-\infty)}\\&\times\int dr_2 dr_3\frac{\delta^2\Sigma(1,1')}{\delta U(2)\delta U(3)}X_n^0(2,2^+)X_0^m(3,3^+) .\end{aligned} \tag{66}$$

(In the above equations $m\neq0$ and $n\neq0$.)

The definition of V_{0n}, given by Eq. (65), is identical to the one given in CTT [Eq. (4a) there]. For the sake of completeness we give here also the definition of the V_{n0} potential by the formula

$$V_{n0}(1,1')=\frac{1}{i}\frac{1}{d_n}\mathcal{L}_{(t_2\to-\infty)}\int dr_2\frac{\delta\Sigma(1,1')}{\delta U(2)}X_0^n(2,2^+) . \tag{67}$$

Using now Eq. (63) in the S-matrix formula [Eq. (2)],

$$S_{nq,mp}=\lim_{\substack{t_1\to\infty\\ t_1'\to-\infty}}\int dr_1 dr_1'\phi_q^*(1)\phi_p(1')X_n^m(1,1') , \tag{68}$$

we obtain

$$S_{nq,mp}=\frac{1}{i}\int d1\,d1'[f_q^{m(-)*}(1')f_p^{(+)}(1)+f_q^{(-)*}(1')\tilde{f}_p^{m(+)}(1)]V_{0n}(1,1')-\int d1\,d1'f_q^{(-)*}(1)f_p^{(+)}(1')V_{mn}(1,1')\ . \quad (69)$$

Here the $f_q^{m(-)*}$ and $f_p^{m(+)}$ functions need to satisfy the equations, respectively,

$$\tilde{f}_p^{m(+)}(1)=\int d3\,d3'G(1,3')f_p^{(+)}(3)V_{m0}(3,3')\ , \quad (70)$$

$$f_q^{m(-)*}(1')=\int d3\,d3'f_q^{(-)*}(3')G(3,1')V_{m0}(3,3')\ . \quad (71)$$

In comparing these latter equations with Eqs. (14) and (15) we can immediately establish the relationship of the present formalism with the one presented in Sec. II. These relations can be given by the formulas

$$V_{0n}(1,1')=\frac{1}{i}\int d2\,d2'\Xi(12,1'2')X_n^0(2',2)\ , \quad (72)$$

$$V_{mn}(1,1')=\int d2\,d2'\Xi(12,1'2')X_n^m(2',2)+\frac{1}{i}\int d2\,d2'd3\,d3'\Xi^{(3)}(123,1'2'3')\times X_n^0(3',3)X_0^m(2',2)\ , \quad (73)$$

and

$$V_{m0}(1,1')=\frac{1}{i}\int d2\,d2'\Xi(12,1'2')X_0^m(2',2)\ . \quad (74)$$

In Sec. II we defined the first-order theory by the approximations

$$\Xi(12,1'2')=-i\delta(1-1')\delta(2-2')V(1-2)+i\delta(1-2')\delta(1'-2)V(1-1')\equiv\tilde{V}(12,1'2')\ , \quad (75a)$$

$$\Xi^{(3)}(123,1'2'3')\equiv 0\ , \quad (75b)$$

and by using $G\equiv G_{\rm HF}$ in Eqs. (70) and (71). Thus we can obtain the fundamental equations of the first-order theory in the new formulation. The above approximations give for the optical coupling potentials

$$V_{0n}^{\rm FOMBT}(1,1')=-\delta(1-1')\int d2\,V(1-2)X_n^0(2,2^+)+V(1-1')X_n^0(1,1'^+)\ , \quad (76)$$

$$F_{mn}^{\rm FOMBT}(1,1')=-i\delta(1-1')\int d2\,V(1-2)X_n^m(2,2^+)+iV(1-1')X_n^m(1,1'^+)\ , \quad (77)$$

$$V_{m0}^{\rm FOMBT}(1,1')=-\delta(1-1')\int d2\,V(1-2)X_0^m(2,2^+)+V(1-1')X_0^m(1,1'^+)\ . \quad (78)$$

If we use these potentials in Eqs. (69)–(71) along with the $G\approx G_{\rm HF}$, $f_p^{(+)}\approx f_p^{(+)\rm HF}$, and $f_q^{(-)}\approx f_q^{(-)\rm HF}$ approximations, we recover FOMBT as defined in Sec. II. Thus the S matrix in FOMBT is obtained by the form [using the above approximations in Eq. (69)],

$$S_{nq,mp}^{\rm FOMBT}=i\int d1\,d2\,f_q^{m(-)*}(1)f_p^{(+)}(1)V(1-2)X_n^0(2,2^+)+i\int d1\,d2f_q^{(-)*}(1)\tilde{f}_p^{m(+)}(1)V(1-2)X_n^0(2,2^+)-i\int d1\,d2\,f_q^{m(-)*}(1)f_p^{(+)}(2)V(1-2)X_n^0(1,2^+)-i\int d1\,d2\,f_q^{(-)*}(1)\tilde{f}_p^{m(+)}(2)V(1-2)X_n^0(1,2^+)+i\int d1\,d2\,f_q^{(-)*}(1)f_p^{(+)}f_p^{(+)}(1)V(1-2)X_n^m(2,2^+)-i\int d1\,d2\,f_q^{(-)*}(1)f_p^{(+)}(2)V(1-2)X_n^m(1,2^+)\ . \quad (79)$$

This form is identical to that given by Eq. (24).

IV. FUNDAMENTAL EQUATIONS OF SECOND-ORDER MANY-BODY THEORY

In this section we shall elaborate on the second-order formulas, analyze the physical meaning of some of the second-order terms, and establish the connection of many-body theory to the distorted wave approximation.

Here we shall define SOMBT by the following approximation for Σ [see CTT Eq. (5)]:

$$\Sigma^{\rm SOMBT}(1,1')=-\frac{Z}{|\bar{r}_1|}\delta(1-1')-U(1)\delta(1-1')-i\delta(1-1')\int d2\,V(1-2)G(2,2^+)+iV(1-1')G(1,1'^+)+\int d2\,d3\,V(1-2)R_{\rm RPA}(32,3^+2^+)V(3-1')G(1,1')-\int d2\,d3\,V(1-2)R_{\rm RPA}(32,1'^+2^+)V(3-1')G(1,3) \quad (80)$$

where Σ and G are connected by the Dyson equation [see Eq. (1) in CTT] and $R_{\rm RPA}$ is defined as [see Eq. (8a) in CTT]

$$R_{\rm RPA}(12,1'2^+)=\frac{\delta G_{\rm HF}(1,1')}{\delta U(2)}\ . \quad (81)$$

Using $\Sigma^{\rm SOMBT}$ in Eq. (66) we obtain

$$
\begin{aligned}
V_{mn}^{\mathrm{SOMBT}}(1,1')=&-i\delta(1-1')\int d2\, V(1-2)X_n^m(2,2^+)+iV(1-1')X_n^m(1,1'^+)\\
&-i\int d2\,d3\, V(1-2)R_n^m(32,3^+2^+)V(3-1')G(1,1')\\
&+i\int d2\,d3\, V(1-2)R_n^m(32,1'^+2^+)V(3-1')G(1,3)\\
&-i\int d2\,d3\, V(1-2)R_n^0(32,3^+2^+)V(3-1')X_0^m(1,1')\\
&+i\int d2\,d3\, V(1-2)R_n^0(32,1'^+2^+)V(3-1')X_0^m(3,1')\\
&+\int d2\,d3 V(1-2)R(32,3^+2^+)V(3-1')X_n^m(1,1')\\
&-\int d2\,d3\, V(1-2)R(32,1'^+2^+)V(3-1')X_n^m(1,3)\ ,
\end{aligned}
\tag{82}
$$

where we have introduced the R_n^0 and R_n^m quantities by the definitions

$$
R_n^0(12,1'2^+)=\frac{1}{d_n}\mathcal{L}_{(t_3\to\infty)}\int dr_3\frac{\delta R(12,1'2^+)}{\delta U(3)}X_n^0(3,3^+)\ ,
\tag{83}
$$

$$
R_n^m(12,1'2^+)=\frac{1}{d_n}\frac{1}{d_m}\mathcal{L}_{(t_3\to\infty)}\mathcal{L}_{(t_4\to-\infty)}\int dr_3dr_4\frac{\delta^2R(12,1'2^+)}{\delta U(3)\delta U(4)}X_n^0(3,3^+)X_0^m(4,4^+)\ .
\tag{84}
$$

From the Schwinger relations (see the Appendix) we obtain the following expressions for the R_n and R_n^m quantities:

$$
R_n(12,1'2^+)=i\langle n|T[\psi^\dagger(1')\psi(1)\psi^\dagger(2^+)\psi(2)]|0\rangle+X_n^0(1,1')G(2,2^+)+X_n^0(2,2^+)G(1,1')
\tag{85}
$$

and

$$
\begin{aligned}
R_n^m(12,1'2^+)=&\langle n|T[\psi(1)\psi^\dagger(1')\psi^\dagger(2^+)\psi(2)]|m\rangle+iX_n^m(1,1')G(2,2^+)+iX_n^m(2,2^+)G(1,1')\\
&+X_n^0(2,2^+)X_0^m(1,1')+\delta_{n,m}[R(12,1'2^+)-G(1,1')G(2,2^+)]\ .
\end{aligned}
\tag{86}
$$

In order to establish a connection between the present many-body theory and DWA we shall consider now only those terms in V_{mn}^{SOMBT} that contain the R_n^m quantity, i.e., the third and fourth terms on the right-hand side of Eq. (82).

Let us separate out the following two terms from R_n^m (assuming that $n\neq m$):

$$
\begin{aligned}
R_n^{m,i}(12,1'2^+)=&\langle n|T[\psi(1)\psi^\dagger(1')]|m\rangle\langle m|\psi^+(2^+)\psi(2)|m\rangle\Theta(t_1-t_2)\Theta(t_1'-t_2)\\
&+\langle n|\psi^\dagger(2)\psi(2)|m\rangle\langle m|T[\psi(1)\psi^\dagger(1')]|m\rangle\Theta(t_2-t_1)\Theta(t_2-t_1')
\end{aligned}
\tag{87a}
$$

and

$$
\begin{aligned}
R_n^{m,f}(12,1'2^+)=&\langle n|T[\psi(1)\psi^\dagger(1')]|n\rangle\langle n|\psi^\dagger(2^+)\psi(2)|m\rangle\Theta(t_1-t_2)\Theta(t_1'-t_2)\\
&+\langle n|\psi^\dagger(2)\psi^{(2)}|n\rangle\langle n|T[\psi(1)\psi^\dagger(1')]|m\rangle\Theta(t_2-t_1)\Theta(t_2-t_1')\ ,
\end{aligned}
\tag{87b}
$$

where $\Theta(t)$ is the usual step function. If we use now $1'^+$ on the left-hand side of Eqs. (87a) and (87b), we obtain

$$
R_n^{m,i}(12,1'^+2^+)=X_n^m(1,1'^+)\rho_m(2)\Theta(t_1-t_2)+X_n^m(2,2^+)\rho_m(1,1'^+)\Theta(t_2-t_1)
\tag{88a}
$$

and

$$
R_n^{m,f}(12,1'^+2^+)=\rho_n(1,1'^+)X_n^m(2,2^+)\Theta(t_1-t_2)+\rho_n(2)X_n^m(1,1'^+)\Theta(t_2-t_1)\ ,
\tag{88b}
$$

where we have introduced the excited-state density and density matrices by the definitions

$$
\rho_m(1)=\langle m|\psi^\dagger(1)\psi(1)|m\rangle
\tag{89}
$$

and

$$
\rho_m(1,1'^+)=\langle m|\psi^\dagger(1'^+)\psi(1)|m\rangle\ .
\tag{90}
$$

We note here that on the right-hand side of Eq. (82), $R_n^m(12,1'2^+)$ appears with $1'\equiv1'^+$ (i.e., $t_1'=t_1+\varepsilon$) and we can write $R_n^m(12,1'2^+)$ in the form using Eq. (86) (and taking again the $n\neq m$ case).

$$
\begin{aligned}
R_n^m(12,1'^+2^+)=&\sum_{k\neq m,n}\langle n|T[\psi(1)\psi^\dagger(1'^+)]|k\rangle\langle k|\psi^\dagger(2)\psi(2)|m\rangle\Theta(t_1-t_2)\\
&+\sum_{k\neq m,n}\langle n|\psi^\dagger(2)\psi(2)|k\rangle\langle k|T[\psi(1)\psi^\dagger(1'^+)]|m\rangle\Theta(t_2-t_1)\\
&+R_n^{m,i}(12,1'^+2^+)+R_n^{m,f}(12,1'^+2^+)+iX_n^m(1,1'^+)G(2,2^+)\\
&+iX_n^m(2,2^+)G(1,1'^+)+X_n^0(2,2^+)X_0^m(1,1'^+)\quad(n\neq m)\ .
\end{aligned}
\tag{91}
$$

When the spectral representation of R_n^m, given by Eqs. (87), (88), and (91), is used in Eq. (82) terms result that can be represented by Feynman-like diagrams as shown in Fig. 4, where the second-order terms on the right-hand side of Eq. (82) are shown. In order to represent the $X_0^m(1,1')$ and $X_n^m(1,1')$ expressions diagrammatically we used the lowest-order direct form expression for them in the form

$$X_0^m(1,1')=\int d2\,d3\,G(1,2)G(2,1')V(2-3)X_0^m(3,3^+)$$

and

$$X_n^m(1,1')=\int d2\,d3\,G(1,2)G(2,1')V(2-3)X_n^m(3,3^+)\ .$$

Therefore these terms actually appear to be third-order terms in Fig. 4.

A physical analysis will show that the first and second term on the right-hand side of Eq. (91) describe transition-polarization effects, whereas the other terms together describe initial-and final-state effects. Here we shall consider only these latter effects. Thus let us assume that we substitute

$$R_n^{m,i,f}(12,1'^+2^+)=R_n^{m,i}(12,1'^+2^+)+R_n^{m,f}(12,1'^+2^+)+iX_n^m(1,1'^+)G(2,2^+)+X_n^m(2,2^+)G(1,1') \tag{92}$$

for $R_n^m(12,1'^+2^+)$ on the right-hand side of Eq. (82). Then we obtain for the third and fourth terms on the right-hand side of Eq. (82),

$$\begin{aligned}V_{m,n}^{(2)i,f}(1,1')=&-i\int d2\,d3\,V(1-2)X_n^m(3,3^+)\rho_m(2)V(3,1')\Theta(t_3-t_3)G(1,1')\\&-i\int d2\,d3\,V(1-2)X_n^m(2,2^+)\rho_m(3)V(3-1')\Theta(t_2-t_3)G(1,1')\\&+i\int d2\,d3\,V(1-2)X_n^m(3,1'^+)\rho_m(2)V(3-1')\Theta(t_3-t_2)G(1,3)\\&+i\int d2\,d3V(1-2)X_n^m(2,2^+)\rho_m(3,1'^+)V(3-1')\Theta(t_2-t_3)G(1,3)\\&+i\int d2\,d3\,V(1-2)X_n^m(3,3^+)\rho_0(2)V(3-1')G(1,1')\\&-i\int d2\,d3\,V(1-2)X_n^m(3,1'^+)\rho_0(2)V(3-1')G(1,3)\\&+i\int d2\,d3\,V(1-2)X_n^m(2,2^+)\rho_0(3)V(3-1')G(1,1')\end{aligned}$$

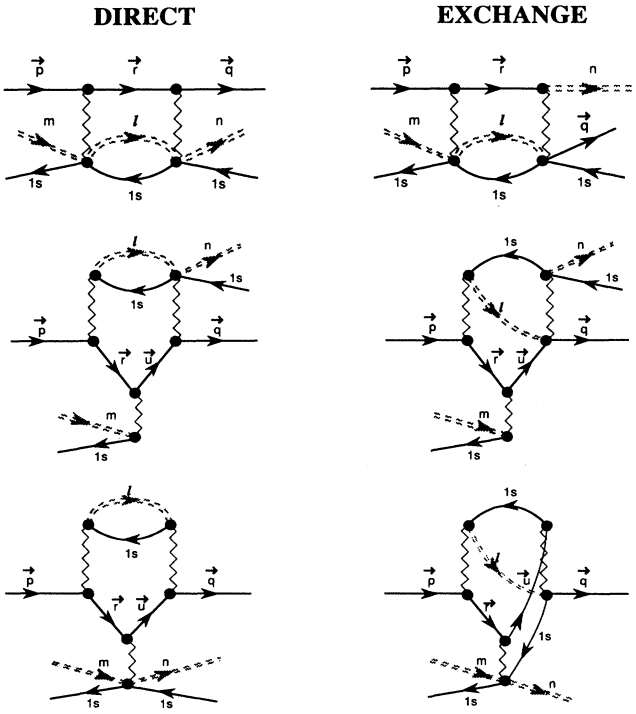

FIG. 4. Feynman-type diagrams to illustrate the physical effects included in SOMBT for excitation from excited states. Notation is the same as in Fig. 2.

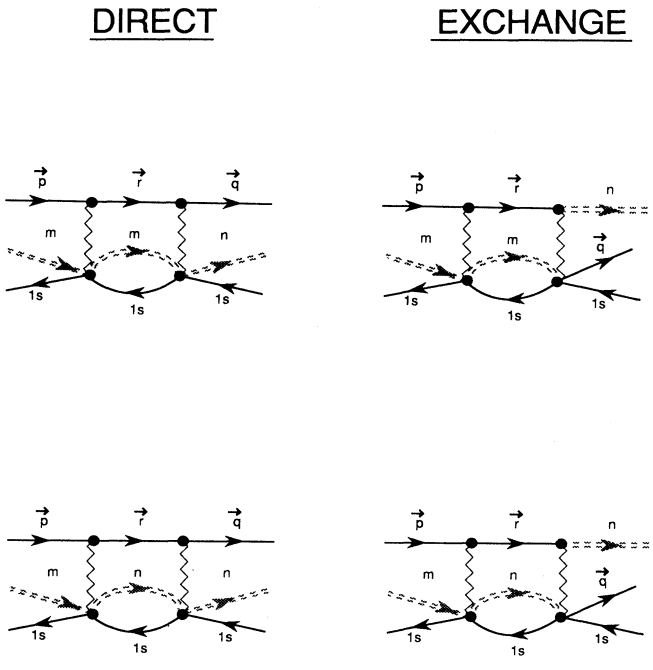

FIG. 5. Initial- and final-state interaction second-order diagrams.

$$-i\int d2\,d3\,V(1-2)X_n^m(2,2^+)\rho_0(3,1'^+)V(3-1')G(1,3)$$
$$-i\int d2\,d3\,V(1-2)\rho_n(3)X_n^m(2,2^+)V(3-1')\Theta(t_3-t_2)G(1,1')$$
$$-i\int d2\,d3\,V(1-2)\rho_n(2)X_n^m(3,3^+)V(3-1')\Theta(t_2-t_3)G(1,1')$$
$$+i\int d2\,d3\,V(1-2)\rho_n(3,1'^+)X_n^m(2,2^+)V(3-1')\Theta(t_3-t_2)G(1,3)$$
$$+i\int d2\,d3\,V(1-2)\rho_n(2)X_n^m(3,1'^+)V(3-1')\Theta(t_2-t_3)G(1,3) \tag{93}$$

where we have introduced the ground-state density $\rho_0(1)$ and ground-state density matrix $\rho_0(1,1'^+)$ via the definitions, respectively,

$$\rho_0(1)=\langle\Psi_0|\psi^\dagger(1)\psi(1)|\Psi_0\rangle\ , \tag{94}$$

$$\rho_0(1,1'^\dagger)=\langle\Psi_0|\psi^\dagger(1'^+)\psi(1)|\Psi_0\rangle\ . \tag{95}$$

On the right-hand side of Eq. (93) integration for the t_2 and t_3 time variables is implied. However, since the $V(1-2)$ and $V(3-1')$ potentials contain $\delta(t_1-t_2)$ and $\delta(t_3-t_1')$ factors, respectively, those integrals can be executed immediately and the result is the $t_2=t_1$ and $t_3=t_1'$ contraction. As a result, every term on the right-hand side contains the $\Theta(t_1-t_1')$ or the $\Theta(t_1-t_1')$ factor. Now, the $G(1,1')\Theta(t_1-t_1')$ term describes forward propagation in time from t_1' to t_1 and $G(1,1')\Theta(t_1'-t_1)$ describes "backwards propagation in time." In our case these latter terms are negligible and therefore $V_{m,n}^{(2)i,f}$ can be written to a good approximation,

$$V_{m,n}^{(2)i,f}(1,1')\approx -i\int d2\,d3\,V(1-2)X_n^m(2,2^+)[\rho_m(3)-\rho_0(3)]\Theta(t_2-t_3)V(3-1')G(1,1')$$
$$+i\int d2\,d3\,V(1-2)X_n^m(2,2^+)[\rho_m(3,1'^+)-\rho_0(3,1'^+)]\Theta(t_2-t_3)V(3-1')G(1,3)$$
$$-i\int d2\,d3\,V(1-2)[\rho_n(2)-\rho_0(2)]X_n^m(3,3^+)\Theta(t_2-t_3)V(3-1')G(1,1')$$
$$+i\int d2\,d3\,V(1-2)[\rho_n(2)-\rho_0(2)]X_n^m(3,1'^+)\Theta(t_2-t_3)V(3-1')G(1,3)\ . \tag{96}$$

If we use this expression in the S-matrix formula [Eq. (69)] we obtain the following expression:

$$S_{nq,mp}^{(2)i,f}=\int d1\,d1'f_q^{(-)*}(1)f_p^{(+)}(1')V_{m,n}^{(2)i,f}(1,1')$$
$$=i\int d1\,d1'd2\,d3\,f_q^{(-)*}(1)V(1-2)X_n^m(2,2^+)[\rho_m(3)-\rho_0(3)]\Theta(t_1-t_1')V(3-1')G(1,1')f_p^{(+)}(1')$$
$$-i\int d1\,d1'd2\,d3\,f_q^{(-)*}(1)V(1-2)X_n^m(2,2^+)[\rho_m(3,1'^+)-\rho_0(3,1'^+)]\Theta(t_1-t_1')V(3-1')G(1,3)f_p^{(+)}(1')$$
$$+i\int d1\,d1'd2\,d3\,f_q^{(-)*}(1)V(1-2)[\rho_n(2)-\rho_0(2)]X_n^m(3,3^+)\Theta(t_1-t_1')V(3-1')G(1,1')f_p^{(+)}(1')$$
$$-i\int d1\,d1'd2\,d3\,f_q^{(-)*}(1)V(1-2)[\rho_n(2)-\rho_0(2)]X_n^m(3,1'^+)\Theta(t_1-t_1')V(3-1')G(1,3)f_p^{+}(1')\ . \tag{97}$$

The first term on the right-hand side is represented by the Feynman-like diagram shown in Fig. 5(a), whereas the third and fourth terms are represented by diagrams shown in Figs. 5(c) and 5(d), respectively. It will be convenient to introduce the static-exchange (SE) potential of state m and the static (S) potential of state n by the expressions, respectively

$$\Sigma_m^{\rm SE}(1,1')=\delta(1-1')\int d2\,V(1-2)\rho_m(2)-V(1-1')\rho_m(1,1'^+)\ , \tag{98}$$

$$\Sigma_n^{\rm S}(1,1')=\delta(1-1')\int d2\,V(1-2)\rho_n(2)\ . \tag{99}$$

Let us add now the first-order direct excitation term [the fifth term on the right-hand side of Eq. (97)] to the first and second terms on the right-hand side of Eq. (97) to give

$$i\int d1\,d2\,f_q^{(-)*}(1)f_p^{(+)}(1)V(1-2)X_n^m(2,2^+)+i\int d1\,d1'd2\,d3\,f_q^{(-)*}(1)V(1-2)$$
$$\times X_n^m(2,2^+)[\Sigma_m^{\rm SE}(3,1'^+)-\Sigma_{\rm HF}(3,1'^+)]\Theta(t_1-t_3)G(1,3)f_p^{(+)}(1')\ , \tag{100}$$

where we used Eq. (98). Equation (100) contains the following expression:

$$f_p^{(+)}(1)+\int d1'd3\, G(1,3)[\Sigma_m^{\mathrm{SE}}(3,1'^+)-\Sigma_{\mathrm{HF}}(3,1'^+)] \times f_p^{(+)}(1')\Theta(t_1-t_3)\ . \quad (101)$$

This expression appears to be the first two terms of a perturbation expansion of an orbital $\phi_p^{(m)(+)}(1)$ defined by the integral equation

$$\phi_p^{(m)(+)}(1)=f_p^{(+)}(1) + \int d1'd3\, G(1,3)\Theta(t_1-t_3) \times[\Sigma_m^{\mathrm{SE}}(3,1'^+)-\Sigma_{\mathrm{HF}}(3,1'^+)] \times\phi_p^{(m)(+)}(1')\ . \quad (102)$$

If additional terms from Eq. (102) are obtained in the perturbation expansion of $\phi_p^{(m)(+)}(1)$ they contribute S-matrix elements that are represented diagramatically in Figs. 6(a) and 6(b). When all such diagrams are summed up to infinite order the resulting sum of S-matrix elements can be represented by just one (first-order diagram) shown in Fig. 6(c). Evidently $\phi_p^{(m)(+)}(1)$ represents a distorted-wave orbital calculated in the static-exchange field of state m and thus the selective summation of some diagrams bring in exactly the effect that is considered in the distorted wave approximation. Quite analogously the third and fourth terms on the right-hand side of Eq. (97) contain the effect of the static field of the final state n upon the first-order direct- and exchange-excitation terms. When such terms are taken into account up to infinite order the effect of the final state enters the formalism, very similarly as it is done in the DWA.

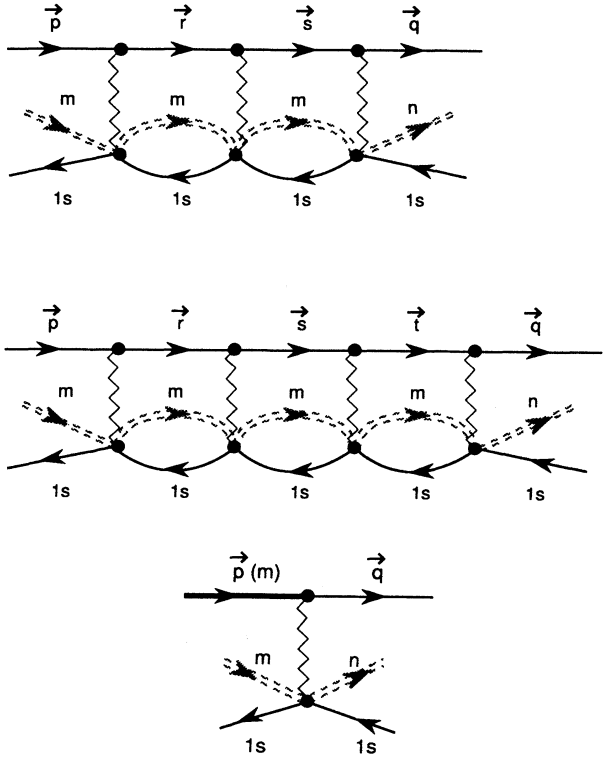

FIG. 6. Higher-order initial-state interaction diagrams and their summation.

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APPENDIX: SCHWINGER-RELATIONS AND OFF-DIAGONAL RESPONSE FUNCTIONS

Let us define the n-electron Green's function by the formula

$$G_n(12\cdots n\ ,1'2'\cdots n') = \frac{1}{i^n}\langle 0|T[\psi(1)\psi(2)\cdots\psi(n)\psi^\dagger(n')\cdots\psi^\dagger(1')]|0\rangle\ ; \quad (A1)$$

then the following equations, called Schwinger relations, hold for the functional derivatives of the one-electron Green's function:

$$R(12,1'2^+)\equiv\frac{\delta G_1(1,1')}{\delta U(2)}=-G_2(12,1'2^+)+G_1(1,1')G_1(2,2^+)\ , \quad (A2)$$

$$R(123,1'2^+3^+)\equiv\frac{\delta^2 G_1(1,1')}{\delta U(3)\delta U(2)} =G_3(123,1'2^+3^+)+R(12,1'2^+)G_1(3,3^+)+R(13,1'3^+)G_1(2,2^+) +R(23,2^+3^+)G_1(1,1')-G_1(1,1')G_1(2,2^+)G_1(3,3^+)\ , \quad (A3)$$

$$R(1234,1'2^+3^+4^+)\equiv\frac{\delta^3 G_1(1,1')}{\delta U(4)\delta U(3)\delta U(2)}$$
$$=-G_4(1234,1'2^+3^+4^+)+G_3(123,1'2^+3^+)G_1(4,4^+)+R(124,1'2^+4^+)G_1(3,3^+)$$
$$+R(12,1'2^+)R(34,3^+4^+)+R(134,1'3^+4^+)G_1(2,2^+)+R(13,1'3^+)R(24,2^+4^+)$$
$$+R(234,2^+3^+4^+)G_1(1,1')+R(23,2^+3^+)R(14,1'4^+)-R(14,1'4^+)G_1(2,2^+)G_1(3,3^+)$$
$$-R(24,2^+3^+)G_1(1,1')G_1(3,3^+)-R(34,3^+4^+)G_1(1,1')G_1(2,2^+)\ . \tag{A4}$$

Throughout this work the $G\equiv G_1$ notation will be used.

If $\mathcal{L}$ refers to the Gell-Mann–Low operator, then we can define the off-diagonal response functions R_n and R_n^m by the equations

$$R_n(12,1'2^+)=\frac{1}{d_n}\mathcal{L}_{(t_3\to\infty)}\int dr_3\frac{\delta^2 G(1,1')}{\delta U(3)\delta U(2)}X_n^0(3,3^+) \tag{A5}$$

and

$$R_n^m(12,1'2^+)=\frac{1}{d_n}\frac{1}{d_m}\mathcal{L}_{(t_4\to-\infty)}\mathcal{L}_{(t_3\to+\infty)}\int dr_3 dr_4\frac{\delta^2 G(1,1')}{\delta U(4)\delta U(3)\delta U(2)}X_n^0(3,3^+)X_0^m(4,4^+)\ . \tag{A6}$$

Using now Eqs. (A2)–(A4) in Eqs. (A5) and (A6) we obtain

$$R_n(12,1'2^+)=i\langle n|T[\psi^\dagger(1')\psi(1)\psi^\dagger(2^+)\psi(2)]|0\rangle+X_n^0(1,1')G(2,2^+)+X_n^0(2,2^+)G(1,1') \tag{A7}$$

and

$$R_n^m(12,1'2^+)=\langle n|T[\psi(1)\psi^\dagger(1')\psi^\dagger(2^+)\psi(2)]|m\rangle+R(1,2,1'2^+)\delta_{nm}+[iX_n^m(1,1')-\delta_{n,m}G_1(1,1')]G(2,2^+)$$
$$+X_n^0(1,1')X_0^m(2,2^+)+iX_n^m(2,2^+)G(1,1')+X_n^0(2,2^+)X_0^m(1,1')\ . \tag{A8}$$

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