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Multiconfiguration relativistic random-phase approximation. Theory

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The relativistic random-phase approximation is generalized to describe excitations of an atomic system having a multiconfiguration ground state. The response of such an atom to an imposed harmonic perturbation is determined by applying the time-dependent variational principle to a multiconfiguration wave function constructed from Dirac orbitals. Terms in the wave function independent of the external field lead to the multiconfiguration Dirac-Fock description of the ground state. Terms proportional to the external field lead to a multiconfiguration generalization of the relativistic random-phase approximation. For the special case of an atom having a ground state with two electrons coupled to $J=0$ outside of closed shells, we write out in detail equations for the configuration weights and for the electronic orbitals. These equations are expanded in a suitable basis to give expressions for the excitation probabilities. An angular momentum analysis is carried out leading to a set of coupled algebraic equations for the configuration weights and a set of radial differential equations for the electronic orbitals.

I. INTRODUCTION

The relativistic random-phase approximation (RRPA) has been employed in the recent past to describe photoexcitation and photoionization processes in atoms and ions of high nuclear charge.[1,2] For closed-shell systems, such as heavy noble gas atoms, where the ground state is well isolated from the excited states, applications of the RRPA have been remarkably successful. For other closed-shell systems, such as alkaline-earth atoms, which have low-lying excited states, such applications have been less successful, owing to the importance of two-electron excitations which are omitted in the RRPA. To date there have been no applications of the RRPA to open-shell systems, since the RRPA is based on a single-configuration reference state and is appropriate only for a description of excitations of closed-shell systems.

It is the purpose of this paper to develop a generalization of the RRPA based on a multiconfiguration reference state which is suitable for treating photoexcitation and photoionization of closed-shell and certain open-shell systems of high nuclear charge. The approach adopted here is in the spirit of that recently employed by Dalgaard[3] to generalize the nonrelativistic time-dependent Hartree-Fock theory. Theoretical methods equivalent to those of Dalgaard have also been developed recently by Yeager and Jørgensen[4] from an equation-of-motion point of view. These methods have already been applied with a high degree of success to a number of nonrelativistic atomic and molecular systems.[4]

Our calculations are based on an approximate relativistic Hamiltonian

$$H(t)=H+V(t)\ , \tag{1.1}$$

where

$$H=\sum_{n=1}^{N} h_n+\sum_{n<m}^{N} v_{nm}\ , \tag{1.2}$$

$$V(t)=v_+ e^{-i\omega t}+v_- e^{i\omega t}\ , \tag{1.3}$$

with

$$v_\pm=\sum_{n=1}^{N} v_{n\pm}\ , \tag{1.4}$$

and

$$v_{nm}=e^2/r_{nm}\ . \tag{1.5}$$

In Eq. (1.2) h_n is a single-electron Dirac Hamiltonian, while in Eq. (1.1), $V(t)$ is an external potential which induces transitions between atomic states. The time-independent part of the Hamiltonian H is assumed to consist of a single-particle Dirac term and a Coulomb term. The Breit interaction is not considered here but may be easily included in the calculation if required. Since the equations resulting from our analysis will be reduced to single-particle Dirac equations describing perturbed orbitals, the problem of "continuum dissolution"[5,6] associated with the Hamiltonian (1.2)

does not arise in the present theory.

Our point of departure is the time-dependent variational principle.[7,8] We describe the N-electron system as a superposition of configuration wave functions with time-dependent weights. Since the external perturbation may have components with nonvanishing angular momentum and with odd parity, the atomic wave function contains terms of mixed angular momentum and parity. Applying the variational principle we derive time-dependent multiconfiguration Dirac-Fock equations describing the response of the atom to the external field. Terms independent of the external field lead to the usual stationary multiconfiguration Dirac-Fock (MCDF) description of an atomic state.[9,10] Those terms proportional to the external field lead to equations describing the linear response of the atomic state to the external field; in the sequel we refer to these linear response equations as the multiconfiguration relativistic random-phase approximation (MCRRPA) equations. If we start from a single-configuration reference state, the MCRRPA equations reduce to the usual RRPA equations. The MCRRPA equations may alternatively be derived from an equation-of-motion point of view.[11]

A general version of the MCRRPA equations which applies to either open-shell or closed-shell atoms is written down in Sec. II. These general equations may be greatly simplified in specific cases. In Sec. III, we illustrate how this simplification is achieved for excitations of the ground state of atoms such as alkaline earths which have two electrons outside of a closed core. For such two-electron atoms, we write out the detailed MCRRPA equations describing perturbed electronic orbitals.

The MCRRPA equations derived in Sec. III are linear equations which can be analyzed on a suitably chosen basis. In Sec. IV, we describe the matrix form of the equations obtained from such an analysis. From the matrix form of the MCRRPA equations we obtain the normalization conditions for perturbed orbitals and we derive expressions for excitation probabilities in terms of the external field.

In Sec. V we carry out the angular momentum reduction of the MCRRPA equations for the case of two-electrons atoms. A set of coupled radial differential equations for perturbed orbitals and a set of coupled algebraic equations for the perturbed weight coefficients are derived. The coupled equations obtained in Sec. V are similar in structure to the radial MCDF equations.

Numerical solutions of the equations for several low-lying states of the Be-like ions have already been carried out,[12] giving excitation energies and transition probabilities in excellent agreement with experiment.

II. THEORY

Let $\Phi(t)$ represent a time-dependent solution to the many-electron Schrödinger equation

$$i\frac{\partial\Phi(t)}{\partial t}=H(t)\Phi(t)\ , \tag{2.1}$$

where $H(t)$ is the approximate relativistic Hamiltonian given in Eqs. (1.1)–(1.5). To obtain approximate solutions to Eq. (2.1) we appeal to the time-dependent variational principle[7,8]

$$\left\langle\delta\Phi(t)\left|i\frac{\partial}{\partial t}-H(t)\right|\Phi(t)\right\rangle=0\ , \tag{2.2}$$

which expresses the condition that the approximation error remain small for all time. Without loss of generality, we write $\Phi(t)$ in the form

$$\Phi(t)=e^{-iEt}\Psi(t)\ , \tag{2.3}$$

Here E is an approximation to a stationary-state energy of the time-independent Hamiltonian H which is obtained from (1.1) when $V(t)$ is neglected. The variational principle can be rewritten in terms of $\Psi(t)$ as

$$\left\langle\delta\Psi(t)\left|E+i\frac{\partial}{\partial t}-H(t)\right|\Psi(t)\right\rangle=0\ . \tag{2.4}$$

We approximate the many-body wave function $\Psi(t)$ by a superposition of configuration functions $\psi_a(t)$,

$$\Psi(t)=\sum_a C_a(t)\psi_a(t)\ , \tag{2.5}$$

where a is a configuration index, and where $C_a(t)$ is a configuration weight coefficient. Using the expansion (2.5), we obtain

$$\left\langle \Psi(t) \left| E+i\frac{\partial}{\partial t}-H(t) \right| \Psi(t) \right\rangle = \sum_{ab} C_a^*(t) \left[EC_b(t)+i\frac{\partial C_b(t)}{\partial t} \right] \langle \psi_a(t) \mid \psi_b(t) \rangle + \sum_{ab} C_a^*(t)C_b(t) \left\langle \psi_a(t) \left| i\frac{\partial}{\partial t}-H(t) \right| \psi_b(t) \right\rangle . \tag{2.6}$$

To maintain the normalization of $\Psi(t)$ for all time, we require

$$\langle \psi_a(t) \mid \psi_b(t) \rangle = \delta_{ab} \tag{2.7}$$

and

$$\sum_a C_a^*(t)C_a(t)=1 . \tag{2.8}$$

The configuration wave functions $\psi_a(t)$ are built up from one-electron orbitals $u_\alpha(t)$. To ensure the orthonormality relation (2.7) we require orthonormality among the one-electron orbitals

$$\langle u_\alpha(t) \mid u_\beta(t) \rangle = \delta_{\alpha\beta} . \tag{2.9}$$

We can simplify Eq. (2.6) by using the orthonormality condition (2.7). Later, when we apply the variational principle we must, of course, introduce Lagrange multipliers to enforce the constraint conditions (2.9). Taking into consideration Eq. (2.7), we find

$$\left\langle \Psi(t) \left| E+i\frac{\partial}{\partial t}-H(t) \right| \Psi(t) \right\rangle = \sum_a C_a^*(t) \left[E+i\frac{\partial}{\partial t} \right] C_a(t) + \sum_{ab} C_a^*(t)C_b(t) \left[\left[i\frac{\partial}{\partial t} \right]_{ab} - H(t)_{ab} \right] , \tag{2.10}$$

where we write symbolically

$$\left[i\frac{\partial}{\partial t} \right]_{ab} \equiv \left\langle \psi_a(t) \left| i\frac{\partial}{\partial t} \right| \psi_b(t) \right\rangle , \tag{2.11}$$

$$H(t)_{ab} \equiv \langle \psi_a(t) \mid H(t) \mid \psi_b(t) \rangle . \tag{2.12}$$

Varying $C_a^*(t)$ and $u_\alpha^\dagger(t)$ in (2.10) according to (2.4) subject to the orthonormality constraint (2.9) we obtain equations for the weight coefficients and orbitals, respectively,

$$\left[E+i\frac{\partial}{\partial t} \right] C_a(t) + \sum_b \left[\left[i\frac{\partial}{\partial t} \right]_{ab} - H(t)_{ab} \right] C_b(t)=0 , \tag{2.13}$$

$$\sum_{ab} C_a^*(t)C_b(t) \left[\delta_\alpha^\dagger \left[i\frac{\partial}{\partial t} \right]_{ab} - \delta_\alpha^\dagger H(t)_{ab} \right] = \sum_\beta \gamma_{\alpha\beta}(t)u_\beta(t) , \tag{2.14}$$

where $\gamma_{\alpha\beta}(t)$ are the Lagrange multipliers, and where we denote functional derivatives with respect to $u_\alpha^\dagger(t)$ as

$$\delta_\alpha^\dagger \left[i\frac{\partial}{\partial t} \right]_{ab} = \frac{\delta}{\delta u_\alpha^\dagger} \left[i\frac{\partial}{\partial t} \right]_{ab} \tag{2.15}$$

and

$$\delta_\alpha^\dagger H(t)_{ab} = \frac{\delta}{\delta u_\alpha^\dagger} H(t)_{ab} . \tag{2.16}$$

Assuming that the Hamiltonian $H(t)$ consists of a time-independent part H describing the many-electron dynamics and a harmonic perturbation $V(t)$ describing interaction with an external field as described in (1.1)–(1.3), we may correspondingly assume a harmonic time dependence for $\Psi(t)$ and write

$$C_a(t)=C_a+[C_a]_+e^{-i\omega t}+[C_a]_-e^{i\omega t}+\cdots , \tag{2.17}$$

$$u_\alpha(t)=u_\alpha+w_{\alpha+}e^{-i\omega t}+w_{\alpha-}e^{i\omega t}+\cdots , \tag{2.18}$$

where $\cdots$ denotes omitted higher-order harmonics. We may also assume that the Lagrange multipliers $\gamma_{\alpha\beta}(t)$ take a similar form

$$\gamma_{\alpha\beta}(t)=\gamma_{\alpha\beta}+[\gamma_{\alpha\beta}]_+e^{-i\omega t}+[\gamma_{\alpha\beta}]_-e^{i\omega t}+\cdots . \tag{2.19}$$

To satisfy the constraints (2.8) and (2.9), we demand

$$\sum_a C_a^*C_a=1 , \tag{2.20}$$

$$\sum_a ([C_a]_\mp^*C_a+C_a^*[C_a]_\pm)=0 , \tag{2.21}$$

$$\langle u_\alpha \mid u_\beta\rangle=\delta_{\alpha\beta} , \tag{2.22}$$

$$\langle w_{\alpha\mp} \mid u_\beta\rangle+\langle u_\alpha \mid w_{\beta\pm}\rangle=0 . \tag{2.23}$$

In the following paragraphs, we impose the stronger conditions

$$\sum_a C_a^*[C_a]_\pm=0 \tag{2.24}$$

$$\langle u_\alpha \mid w_{\beta\pm}\rangle=0 \tag{2.25}$$

to guarantee the relations (2.21) and (2.23). Substituting (2.17)–(2.19) into Eqs. (2.13) and (2.14), and equating coefficients in powers of $e^{\pm i\omega t}$, we obtain zeroth-order and first-order equations governing the many-particle system.

(i) Zeroth order.

$$EC_a-\sum_b [H_{ab}]_0C_b=0 , \tag{2.26}$$

$$\sum_{ab} C_a^*C_b[\delta_\alpha^\dagger H_{ab}]_0-\sum_\beta \gamma_{\alpha\beta}u_\beta=0 , \tag{2.27}$$

(ii) First order.

$$(E\pm\omega)[C_a]_\pm-\sum_b([H_{ab}]_0[C_b]_\pm+[H_{ab}]_\pm C_b)=\sum_b [V_{ab}]_\pm C_b . \tag{2.28}$$

$$\sum_{ab} C_a^*C_b\left\{\left[\delta_\alpha^\dagger\left[i\frac{\partial}{\partial t}\right]_{ab}\right]_\pm-[\delta_\alpha^\dagger H_{ab}]_\pm\right\}-\sum_{ab}([C_a]_\mp^*C_b+C_a^*[C_b]_\pm)[\delta_\alpha^\dagger H_{ab}]_0-\sum_\beta(\gamma_{\alpha\beta}w_{\beta\pm}+[\gamma_{\alpha\beta}]_\pm u_\beta)$$
$$=\sum_{ab} C_a^*C_b[\delta_\alpha^\dagger V_{ab}]_\pm . \tag{2.29}$$

In Eqs. (2.26)–(2.29) we have used square brackets with subscripts to designate the coefficients in powers of $e^{\pm i\omega t}$ in the expansion of various matrix elements:

$$H_{ab}\equiv\langle\psi_a(t)\mid H\mid\psi_b(t)\rangle=[H_{ab}]_0+[H_{ab}]_+e^{-i\omega t}+[H_{ab}]_-e^{i\omega t}+\cdots , \tag{2.30}$$

$$V_{ab}\equiv\langle\psi_a(t)\mid V(t)\mid\psi_b(t)\rangle=[V_{ab}]_+e^{-i\omega t}+[V_{ab}]_-e^{i\omega t}+\cdots , \tag{2.31}$$

$$\delta_\alpha^\dagger\left[i\frac{\partial}{\partial t}\right]_{ab}=\left[\delta_\alpha^\dagger\left[i\frac{\partial}{\partial t}\right]_{ab}\right]_+e^{-i\omega t}+\left[\delta_\alpha^\dagger\left[i\frac{\partial}{\partial t}\right]_{ab}\right]_-e^{i\omega t}+\cdots , \tag{2.32}$$

$$\delta_\alpha^\dagger H_{ab}=[\delta_\alpha^\dagger H_{ab}]_0+[\delta_\alpha^\dagger H_{ab}]_+e^{-i\omega t}+[\delta_\alpha^\dagger H_{ab}]_-e^{i\omega t}+\cdots , \tag{2.33}$$

$$\delta_\alpha^\dagger V_{ab}=[\delta_\alpha^\dagger V_{ab}]_+e^{-i\omega t}+[\delta_\alpha^\dagger V_{ab}]_-e^{i\omega t}+\cdots . \tag{2.34}$$

In (2.31) and (2.34), the coefficients are given explicitly by

$$[V_{ab}]_\pm=\langle\psi_a\mid v_\pm\mid\psi_b\rangle=(v_\pm)_{ab} , \tag{2.35}$$

$$[\delta_\alpha^\dagger V_{ab}]_\pm=\delta_\alpha^\dagger(v_\pm)_{ab} . \tag{2.36}$$

To arrive at (2.26)–(2.29), we have used

$$\left[\left[i\frac{\partial}{\partial t}\right]_{ab}\right]_0=0 \tag{2.37}$$

and

$$\left[\left[i\frac{\partial}{\partial t}\right]_{ab}\right]_\pm=0 . \tag{2.38}$$

which can easily be shown by taking into account (2.25). The zeroth-order equations [(2.26) and (2.27)] are just MCDF equations for the unperturbed orbitals u_α and unperturbed weight coefficients C_a. The parameter E is the MCDF approximation to the energy of an atomic stationary state.

The first-order equations [(2.28) and (2.29)] are the MCRRPA equations describing the response of the atom to the external perturbation $v_{\pm}$. Homogeneous MCRRPA equations obtained by omitting the perturbing terms $v_{\pm}$ on the right-hand sides of (2.28) and (2.29) describe the free oscillations of the atomic system. The parameter ω is a natural frequency of oscillation of the system.

III. MCRRPA ORBITAL EQUATIONS

To describe the general procedure for reducing the multiconfiguration equations [(2.26)–(2.29)] to orbital form without invoking complicated mathematical manipulations, we confine our treatment to systems such as the alkaline earths, which have two particles outside of a closed core. Since we have in mind applications to photoexcitation and photoionization, we restrict our attention to excitations from the ground state of such systems.

We place no *a priori* limit on how many configurations are to be included in the expansion (2.5); however, we do restrict our choice to configurations which can be constructed from a given set of orbitals. For example, to describe the beryllium atom, we consider only $1s_{1/2}$, $2s_{1/2}$, $2p_{1/2}$, and $2p_{3/2}$ orbitals. The configuration functions $\psi_a(t)$ will then consist of all possible multiplets with different angular momenta and parities. For atoms with two electrons outside of closed shells, the set of orbitals will consist of core orbitals (e.g., $1s_{1/2}$) which describe closed shells in all configurations and valence orbitals (e.g., $2s_{1/2}$, $2p_{1/2}$, $2p_{3/2}$) which have different occupation numbers in different configurations. Of course the designation of an orbital $u_\alpha(t)$ by quantum numbers n_α and $\kappa_\alpha=(j_\alpha, l_\alpha)$ is somewhat artificial since, in view of Eqs. (2.18) and (2.29), the perturbed components $w_{\alpha\pm}$ will be a mixture of terms with different values of κ. In the following paragraphs we adopt the convention that an orbital $u_\alpha(t)$ is referred to by the quantum numbers $\alpha=(n_\alpha,\kappa_\alpha)$ of its unperturbed component.

We refer to a configuration [(closed core) $(n_{a_1}\kappa_{a_1})$ $(n_{a_2}\kappa_{a_2})$]J_a by the configuration index a. Let us consider configurations which can be built up from F distinct valence orbitals. We arrange the possible configurations in an order such that the first F configurations are those with two equivalent valence electrons coupled to zero total angular momentum, viz.,

$$(n_{a_1}\kappa_{a_1})=(n_{a_2}\kappa_{a_2})\equiv(n_a\kappa_a)\ ,$$

and (3.1)

$$J_a=0 \text{ for } a\le F\ .$$

The remaining configurations will have $(n_{a_1}k_{a_1})\neq(n_{a_2}k_{a_2})$ and play a role in describing excitation of the system.

A general configuration wave function is given by

$$|\psi_a(t)\rangle=|(\mathscr{C})(n_{a_1}\kappa_{a_1},n_{a_2}\kappa_{a_2})J_aM_a\rangle\ , \tag{3.2}$$

where $\mathscr{C}$ represents the closed core, or explicitly by

$$\psi_a(t)=N_a\sum_{m_{a_1}m_{a_2}}\langle j_{a_1}m_{a_1}j_{a_2}m_{a_2}|J_aM_a\rangle \times\Theta(ijk\cdots a_1a_2)\ , \tag{3.3}$$

where

$$N_a=\begin{cases}1, & n_{a_1}\kappa_{a_1}\neq n_{a_2}\kappa_{a_2}\ ,\\ \dfrac{1}{\sqrt{2}}, & n_{a_1}\kappa_{a_1}=n_{a_2}\kappa_{a_2}\ ,\end{cases} \tag{3.4}$$

and where $\Theta(ijk\cdots a_1a_2)$ is a Slater determinant composed of orbitals

$$\{u_i(t),u_j(t),u_k(t),\ldots,u_{a_1}(t),u_{a_2}(t)\}\ .$$

Here $i,j,k,\ldots$ refer to core orbitals, and a_1 and a_2 refer to the two valence orbitals. Using (3.3), we can evaluate the matrix element (2.11) as

$$\left[i\frac{\partial}{\partial t}\right]_{ab}=\delta_{ab}\sum_k\left\langle k\left|i\frac{\partial}{\partial t}\right|k\right\rangle+N_aN_b\sum_{\substack{m_{a_1}m_{a_2}\\ m_{b_1}m_{b_2}}}\langle j_{a_1}m_{a_1}j_{a_2}m_{a_2}|J_aM_a\rangle\langle j_{b_1}m_{b_1}j_{b_2}m_{b_2}|J_bM_b\rangle$$
$$\times\left[\delta_{a_2b_2}\left\langle a_1\left|i\frac{\partial}{\partial t}\right|b_1\right\rangle-\delta_{a_2b_1}\left\langle a_1\left|i\frac{\partial}{\partial t}\right|b_2\right\rangle\right.$$
$$\left.+\delta_{a_1b_1}\left\langle a_2\left|i\frac{\partial}{\partial t}\right|b_2\right\rangle-\delta_{a_1b_2}\left\langle a_2\left|i\frac{\partial}{\partial t}\right|b_1\right\rangle\right]\ , \tag{3.5}$$

where the index $k \equiv (n_k \kappa_k m_k)$ is for core orbitals, and the summation $\sum_k$ is over all the core orbitals. The index $a_1 \equiv (n_{a_1} k_{a_1} m_{a_1})$ (and similarly, a_2, b_1, b_2) is for valence orbitals. We have also used the notation

$$\left\langle \alpha \left| i\frac{\partial}{\partial t} \right| \beta \right\rangle = \left\langle \alpha(1,t) \left| i\frac{\partial}{\partial t} \right| \beta(1,t) \right\rangle = \int d^3 r_1 u_\alpha^\dagger(1,t) i\frac{\partial}{\partial t} u_\beta(1,t) \, . \tag{3.6}$$

With the time-independent part (1.2) of the total Hamiltonian, the matrix element (2.30) is given by

$$\begin{aligned} H_{ab} = {} & \delta_{ab} \left[\sum_i h(ii) + \sum_{i<k} V(ik;ik) \right] \\ & + N_a N_b \sum_{\substack{m_{a_1} m_{a_2} \\ m_{b_1} m_{b_2}}} \langle j_{a_1} m_{a_1} j_{a_2} m_{a_2} | J_a M_a \rangle \langle j_{b_1} m_{b_1} j_{b_2} m_{b_2} | J_b M_b \rangle \\ & \times \left[\delta_{a_2 b_2} \left[h(a_1,b_1) + \sum_i V(ia_1;ib_1) \right] - \delta_{a_2 b_1} \left[h(a_1 b_2) + \sum_i V(ia_1;ib_2) \right] \right. \\ & + \delta_{a_1 b_1} \left[h(a_2 b_2) + \sum_i V(ia_2;ib_2) \right] - \delta_{a_1 b_2} \left[h(a_2 b_1) + \sum_i V(ia_2;ib_1) \right] \\ & \left. + V(a_1 a_2; b_1 b_2) \right] , \end{aligned} \tag{3.7}$$

where i and k are core-orbital indices and

$$h(\alpha\beta) = \langle \alpha(1,t) | h_1 | \beta(1,t) \rangle = \int d^3 r_1 u_\alpha^\dagger(1,t) h_1 u_\beta(1,t) \, , \tag{3.8}$$

$$\begin{aligned} V(\alpha\beta;\sigma\lambda) &= \langle \alpha(1,t)\beta(2,t) | V_{12} | \sigma(1,t)\lambda(2,t) \rangle \\ &= \int d^3 r_1 \int d^3 r_2 u_\alpha^\dagger(1,t) u_\beta^\dagger(2,t) V_{12} u_\sigma(1,t) u_\lambda(2,t) \, . \end{aligned} \tag{3.9}$$

Here the operator V_{12} is

$$V_{12} = v_{12}(1 - P_{12}) \tag{3.10}$$

with P_{12} being the permutation operator for particles 1 and 2. Using the explicit expressions (3.5) and (3.7) we can evaluate the functional derivatives (2.32) and (2.33). It is convenient to consider core orbitals and valence orbitals separately.

(a) Core orbital u_k.

$$\delta_k^\dagger \left[i\frac{\partial}{\partial t} \right]_{ab} = \delta_{ab} i\frac{\partial}{\partial t} u_k(t), \tag{3.11}$$

$$\begin{aligned} \delta_k^\dagger H_{ab} = {} & \delta_{ab} \left[h + \sum_i V(ii) \right] u_k(t) \\ & + N_a N_b \sum_{\substack{m_{a_1} m_{a_2} \\ m_{b_1} m_{b_2}}} \langle j_{a_1} m_{a_1} j_{a_2} m_{a_2} | J_a M_a \rangle \langle j_{b_1} m_{b_1} j_{b_2} m_{b_2} | J_b M_b \rangle \\ & \times [\delta_{a_2 b_2} V(a_1 b_1) - \delta_{a_2 b_1} V(a_1 b_2) + \delta_{a_1 b_1} V(a_2 b_2) - \delta_{a_1 b_2} V(a_2 b_1)] u_k(t) \, , \end{aligned} \tag{3.12}$$

where

$$hu_\alpha(t)=h_1 u_\alpha(1,t)\,, \tag{3.13}$$

$$V(\alpha\beta)u_\sigma(t)=\int d^3r_2 u_\alpha^\dagger(2,t)V_{12}u_\beta(2,t)u_\sigma(1,t)$$
$$=\int d^3r_2[u_\alpha^\dagger(2,t)v_{12}u_\beta(2,t)u_\sigma(1,t)-u_\alpha^\dagger(2,t)v_{12}u_\beta(1,t)u_\sigma(2,t)]\,. \tag{3.14}$$

(b) Valence orbital u_α.

$$\delta_\alpha^\dagger\left[i\frac{\partial}{\partial t}\right]_{ab}=N_aN_b\sum_{\substack{m_{a_1}m_{a_2}\\ m_{b_1}m_{b_2}}}\langle j_{a_1}m_{a_1}j_{a_2}m_{a_2}\,|\,J_aM_a\rangle\langle j_{b_1}m_{b_1}j_{b_2}m_{b_2}\,|\,J_bM_b\rangle$$
$$\times i\frac{\partial}{\partial t}[\delta_{\alpha a_1}\delta_{a_2b_2}u_{b_1}(t)-\delta_{\alpha a_1}\delta_{a_2b_1}u_{b_2}(t)+\delta_{\alpha a_2}\delta_{a_1b_1}u_{b_2}(t)-\delta_{\alpha a_2}\delta_{a_1b_2}u_{b_1}(t)]\,, \tag{3.15}$$

$$\delta_\alpha^\dagger H_{ab}=N_aN_b\sum_{\substack{m_{a_1}m_{a_2}\\ m_{b_1}m_{b_2}}}\langle j_{a_1}m_{a_1}j_{a_2}m_{a_2}\,|\,J_aM_a\rangle\langle j_{b_1}m_{b_1}j_{b_2}m_{b_2}\,|\,J_bM_b\rangle$$
$$\times\left[\left[h+\sum_i V(ii)\right][\delta_{\alpha a_1}\delta_{a_2b_2}u_{b_1}(t)-\delta_{\alpha a_1}\delta_{a_2b_1}u_{b_2}(t)+\delta_{\alpha a_2}\delta_{a_1b_1}u_{b_2}(t)-\delta_{\alpha a_2}\delta_{a_1b_2}u_{b_1}(t)]\right.$$
$$\left.+\delta_{\alpha a_1}V(a_2b_2)u_{b_1}(t)+\delta_{\alpha a_2}V(a_1b_1)u_{b_2}(t)\right]\,. \tag{3.16}$$

To obtain further simplification of the MCDF and MCRRPA equations [(2.26)–(2.29)], we need the following zeroth-order and first-order expressions:

$$[h(\alpha\beta)]_0=\int d^3r_1 u_\alpha^\dagger(1)h_1u_\beta(1)\,, \tag{3.17}$$

$$[h(\alpha\beta)]_\pm=\int d^3r_1[w_{\alpha\mp}^\dagger(1)h_1u_\beta(1)+u_\alpha^\dagger(1)h_1w_{\beta\pm}(1)]\,, \tag{3.18}$$

$$[V(\alpha\beta;\sigma\lambda)]_0=\int d^3r_1\int d^3r_2 u_\alpha^\dagger(1)u_\beta^\dagger(2)V_{12}u_\sigma(1)u_\lambda(2)\,, \tag{3.19}$$

$$[V(\alpha\beta;\sigma\lambda)]_\pm=\int d^3r_1\int d^3r_2[w_{\alpha\mp}^\dagger(1)u_\beta^\dagger(2)V_{12}u_\sigma(1)u_\lambda(2)+u_\alpha^\dagger(1)w_{\beta\mp}^\dagger(2)V_{12}u_\sigma(1)u_\lambda(2)$$
$$+u_\alpha^\dagger(1)u_\beta^\dagger(2)V_{12}w_{\sigma\pm}(1)u_\lambda(2)+u_\alpha^\dagger(1)u_\beta^\dagger(2)V_{12}u_\sigma(1)w_{\lambda\pm}(2)]\,, \tag{3.20}$$

$$\left[i\frac{\partial}{\partial t}u_\alpha(t)\right]_0=0\,, \tag{3.21}$$

$$\left[i\frac{\partial}{\partial t}u_\alpha(t)\right]_\pm=\pm\omega w_{\alpha\pm}(1)\,, \tag{3.22}$$

$$[hu_\alpha(t)]_0=h_1u_\alpha(1)\,, \tag{3.23}$$

$$[hu_\alpha(t)]_\pm=h_1w_{\alpha\pm}(1)\,, \tag{3.24}$$

$$[V(\alpha\beta)u_\sigma(t)]_0=\int d^3r_2u_\alpha^\dagger(2)V_{12}u_\beta(2)u_\sigma(1)\,, \tag{3.25}$$

$$[V(\alpha\beta)u_\sigma(t)]_\pm = \int d^3r_2[w^\dagger_{\alpha\mp}(2)V_{12}u_\beta(2)u_\sigma(1)+u^\dagger_\alpha(2)V_{12}w_{\beta\pm}(2)u_\sigma(1)+u^\dagger_\alpha(2)V_{12}u_\beta(2)w_{\sigma\pm}(1)] . \tag{3.26}$$

From (3.21) and (3.22) we can easily show

$$\left[\delta^\dagger_k\left[i\frac{\partial}{\partial t}\right]_{ab}\right]_\pm = \pm\delta_{ab}\omega w_{k\pm}(1) , \tag{3.27}$$

$$\left[\delta^\dagger_\alpha\left[i\frac{\partial}{\partial t}\right]_{ab}\right]_\pm = \pm\delta_{aa}\delta_{ab}\frac{2}{[a]^2}\omega w_{a\pm}, \quad \text{for } a,b,\le F , \tag{3.28}$$

where we have used the notation

$$[a]\equiv\sqrt{2j_a+1} . \tag{3.29}$$

We note also the relation (3.1) and $\kappa_a=(j_a l_a)$. Similarly, we have

$$[V_{ab}]_\pm=\delta_{ab}\sum_i v_\pm(ii)+N_aN_b\sum_{\substack{m_{a_1}m_{a_2}\\ m_{b_1}m_{b_2}}}\langle j_{a_1}m_{a_1}j_{a_2}m_{a_2}\,|\,J_aM_a\rangle\langle j_{b_1}m_{b_1}j_{b_2}m_{b_2}\,|\,J_bM_b\rangle$$
$$\times[\delta_{a_2b_2}v_\pm(a_1b_1)-\delta_{a_2b_1}v_\pm(a_1b_2)+\delta_{a_1b_1}v_\pm(a_2b_2)-\delta_{a_1b_2}v_\pm(a_2b_1)] , \tag{3.30}$$

where

$$v_\pm(\alpha\beta)=\int d^3r_1u^\dagger_\alpha(1)v_{1\pm}u_\beta(1) . \tag{3.31}$$

Its functional derivatives are

$$[\delta^\dagger_k V_{ab}]_\pm=\delta_{ab}v_\pm u_k , \tag{3.32}$$

$$[\delta^\dagger_\alpha V_{ab}]_\pm=N_aN_b\sum_{\substack{m_{a_1}m_{a_2}\\ m_{b_1}m_{b_2}}}\langle j_{a_1}m_{a_1}j_{a_2}m_{a_2}\,|\,J_aM_a\rangle\langle j_{b_1}m_{b_1}j_{b_2}m_{b_2}\,|\,J_bM_b\rangle$$
$$\times v_\pm(\delta_{\alpha a_1}\delta_{a_2b_2}u_{b_1}-\delta_{\alpha a_1}\delta_{a_2b_1}u_{b_2}+\delta_{\alpha a_2}\delta_{a_1b_1}u_{b_2}-\delta_{\alpha a_2}\delta_{a_1b_2}u_{b_1}) , \tag{3.33}$$

where

$$v_\pm u_\alpha=v_{1\pm}u_\alpha(1) . \tag{3.34}$$

We now consider specifically the excitations of atoms with two valence electrons from its $^1S_0$ ground state. We therefore seek the ground-state solution of the zeroth-order equations, i.e., the MCDF equations. The only nonvanishing C_a for the ground state are those with $a\le F$, i.e.,

$$C_a=0, \quad \text{for } a>F . \tag{3.35}$$

By substituting (3.17)—(3.28), (3.32), and (3.33) into (2.27) and (2.29), we obtain MCDF and MCRRPA equations for orbitals.

(a) MCDF.

$$\epsilon_\alpha\Lambda_\alpha u_\alpha+\sum_{ab}C^*_aC_b[\delta^\dagger_\alpha H_{ab}]_0=\sum_{\beta\neq\alpha}\gamma_{\alpha\beta}u_\beta , \tag{3.36}$$

(b) MCRRPA.

$$(\epsilon_\alpha \pm \omega)\Lambda_\alpha w_{\alpha\pm} = \sum_{ab} C_a^* C_b [\delta_\alpha^\dagger H_{ab}]_\pm + \sum_{ab} ([C_a]_\mp^* C_b + C_a^* [C_b]_\pm)[\delta_\alpha^\dagger H_{ab}]_0 + \sum_{\beta\neq\alpha} \gamma_{\alpha\beta} w_{\beta\pm} + \sum_\beta [\gamma_{\alpha\beta}]_\pm u_\beta + \sum_{ab} C_a^* C_b [\delta_\alpha^\dagger V_{ab}]_\pm , \tag{3.37}$$

where the metric Λ_α is defined as

$$\Lambda_\alpha = \begin{cases} \dfrac{2}{[a]^2} C_a^* C_a, & \text{if } \alpha = a, \text{ valence orbital} \\ 1, & \text{if } \alpha = k, \text{ core orbital.} \end{cases} \tag{3.38}$$

We have defined the orbital eigenvalue ϵ_α as

$$\epsilon_\alpha = -\gamma_{\alpha\alpha}/\Lambda_\alpha . \tag{3.39}$$

For computational purposes, (3.36) and (3.37) can be reduced to more convenient forms.

(a) MCDF.

(i) Core orbitals:

$$\epsilon_k u_k + \sum_a C_a^* C_a [\delta_k^\dagger H_{aa}]_0 = \sum_{\beta\neq k} \lambda_{k\beta} u_\beta , \tag{3.40}$$

(ii) Valence orbitals:

$$\epsilon_a u_a + \Lambda_a^{-1} \sum_b C_a^* C_b [\delta_a^\dagger H_{ab}]_0 = \sum_{\beta\neq a} \lambda_{a\beta} u_\beta . \tag{3.41}$$

(b) MCRRPA.

(i) Core orbitals

$$(\epsilon_k \pm \omega) w_{k\pm} = \sum_{a\leq F} C_a^* C_a [\delta_k^\dagger H_{aa}]_\pm + \sum_{a\leq F} ([C_a]_\mp^* C_a + C_a^* [C_a]_\pm)[\delta_k^\dagger H_{aa}]_0 + \sum_{\substack{a\leq F \\ d>F}} (C_a^* [C_d]_\pm [\delta_k^\dagger H_{ad}]_0 + [C_d]_\mp^* C_a [\delta_k^\dagger H_{da}]_0) + \sum_{\beta\neq k} \lambda_{k\beta} w_{\beta\pm} + \sum_\beta [\lambda_{k\beta}]_\pm u_\beta + v_\pm u_k , \tag{3.42}$$

(ii) Valence orbitals:

$$(\epsilon_a \pm \omega) w_{a\pm} = \Lambda_a^{-1} \sum_{b\leq F} \left[C_a^* C_b [\delta_a^\dagger H_{ab}]_\pm + \left[C_a^* [C_b]_\pm - \frac{C_a^*}{C_a} [C_a]_\pm C_b \right] [\delta_a^\dagger H_{ab}]_0 \right] + \Lambda_a^{-1} \sum_{d>F} C_a^* [C_d]_\pm [\delta_a^\dagger H_{ad}]_0 + \sum_{\beta\neq a} \lambda_{a\beta} w_{\beta\pm} + \sum_\beta [\lambda_{a\beta}]_\pm u_\beta + \Lambda_a^{-1} \sum_b C_a^* C_b [\delta_a^\dagger V_{ab}]_\pm . \tag{3.43}$$

In (3.40)–(3.43) we have defined the Lagrange multipliers as

$$\lambda_{\alpha\beta} = \gamma_{\alpha\beta}/\Lambda_\alpha , \tag{3.44}$$

$$[\lambda_{\alpha\beta}]_\pm = [\gamma_{\alpha\beta}]_\pm/\Lambda_\alpha . \tag{3.45}$$

IV. MATRIX FORM OF THE MCRRPA EQUATIONS

To facilitate the discussion of transition probabilities we consider the reduction of the equations of Sec. III to a linear algebraic system. To this end we introduce a complete orthonormal family of Dirac orbitals u_α. The orbitals u_α are required to coincide with the MCDF orbitals derived from (3.40) and (3.41) for core and valence electrons, but, in addition, are required to span the space of possible excited orbitals. If we order the orbitals so that the first f's are core and valence orbitals and the remaining are excited orbitals, then, since the perturbed orbitals $w_{\alpha\pm}$ are orthogonal to the unperturbed core and valence orbitals, by Eq.

(2.25), we may write

$$w_{\alpha+}=\sum_{\mu>f} X_{\alpha\mu}u_\mu,\quad \alpha\le f$$
$$w_{\alpha-}=\sum_{\mu>f} Y^*_{\alpha\mu}u_\mu,\quad \alpha\le f\ . \tag{4.1}$$

In parallel with the expansion (4.1), we may decompose the perturbed weight coefficients $[C_a]_\pm$ from Eqs. (2.17) and (2.28) in terms of eigenvectors of the matrix $[H_{ab}]_0$. If we let $E^{(n)}$ be the nth eigenvalue of $[H_{ab}]_0$ and let $C_a^{(n)}$ be the corresponding eigenvector, then

$$E^{(n)}C_a^{(n)}=\sum_b [H_{ab}]_0 C_b^{(n)}\ . \tag{4.2}$$

The matrix $[H_{ab}]_0$ can be brought to block-diagonal form by ordering the configurations according to total angular momentum and parity. Each block, having a definite value of J and π, will lead to a separate eigenvalue problem for a multiplet which can be constructed from the core and valence MCDF orbitals.

Taking into consideration our convention (3.1) for ordering the configurations, the first F values of the configuration index a describe a multiplet with $J_a=0$ and $\pi_a=+1$. Since the ground state has the lowest energy in this multiplet, we may write

$$E^{(1)}=E \tag{4.3}$$

for the lowest eigenvalue, and correspondingly

$$C_a^{(1)}=\begin{cases} C_a, & a=1,\ldots,F \\ 0, & a>F\ . \end{cases} \tag{4.4}$$

The remaining eigenvectors of (4.2) for the ground-state multiplet also form F-dimensional vectors, but these excited $J_a=0$, $\pi_a=+1$ vectors are orthogonal to the F-dimensional vector C_a. Now in view of the orthogonality requirement for weight coefficients (2.24), we may expand the perturbed weights $[C_a]_\pm$ in terms of the eigenvector of (4.2) as

$$[C_a]_+=\sum_{n>1}\xi_n C_a^{(n)}\ ,$$
$$[C_a]_-=\sum_{n>1}\eta_n^* C_a^{(n)}\ . \tag{4.5}$$

Substituting the expansions (4.1) and (4.5) into the MCRRPA equations (3.37), we obtain

$$\omega\Lambda_\alpha X_{\alpha\mu}=\sum_{\substack{\beta\le f\\ \nu>f}}[P_{\alpha\mu,\beta\nu}X_{\beta\nu}+Q_{\alpha\mu,\beta\nu}Y_{\beta\nu}] +\sum_{n>1}[P_{\alpha\mu,n}\xi_n+Q_{\alpha\mu,n}\eta_n]+\Lambda_\alpha\langle v_+\rangle_{\mu\alpha}\ , \tag{4.6}$$

$$-\omega\Lambda_\alpha Y_{\alpha\mu}=\sum_{\substack{\beta\le f\\ \nu>f}}[Q^*_{\alpha\mu,\beta\nu}X_{\beta\nu}+P^*_{\alpha\mu,\beta\nu}Y_{\beta\nu}] +\sum_{n>1}[Q^*_{\alpha\mu,n}\xi_n+P^*_{\alpha\mu,n}\eta_n]+\Lambda_\alpha\langle v_-\rangle^*_{\mu\alpha}\ . \tag{4.7}$$

Similar equations for the expansion coefficients ξ_n and η_n can be derived using Eqs. (4.1), (4.5), and (2.28):

$$\omega\xi_n=\sum_{\beta\le f,\mu>f}[P_{n,\beta\mu}X_{\beta\mu}+Q_{n,\beta\mu}Y_{\beta\mu}] +P_{n,n}\xi_n+(v_+)_n\ , \tag{4.8}$$

$$-\omega\eta_n=\sum_{\beta\le f,\mu>f}[Q^*_{n,\beta\mu}X_{\beta\mu}+P^*_{n,\beta\mu}Y_{\beta\mu}] +P^*_{n,n}\eta_n+(v_-)_n\ . \tag{4.9}$$

The notation used in Eqs. (4.6)–(4.9) is as follows:

$$P_{\alpha\mu,\beta\nu}=\sum_{ab}C_a^*C_b\int d^3r\,u_\mu^\dagger(r)[\delta_\alpha^\dagger H_{ab}]_+ +\gamma_{\alpha\beta}\delta_{\mu\nu}\ , \tag{4.10}$$

with $w_{\beta+}$ replaced by u_ν;

$$Q_{\alpha\mu,\beta\nu}=\sum_{ab}C_a^*C_b\int d^3r\,u_\mu^\dagger(r)[\delta_\alpha^\dagger H_{ab}]_+\ , \tag{4.11}$$

with $w^\dagger_{\beta-}$ replaced by $u^\dagger_\nu$;

$$P_{\alpha\mu,n}=\sum_{a,b}C_a^*C_b^{(n)}\int d^3r\,u_\mu^\dagger(r)[\delta_\alpha^\dagger H_{ab}]_0\ , \tag{4.12}$$

$$Q_{\alpha\mu,n}=\sum_{a,b}C_a^{(n)*}C_b\int d^3r\,u_\mu^\dagger(r)[\delta_\alpha^\dagger H_{ab}]_0\ , \tag{4.13}$$

$$P_{n,\beta\nu}=P^*_{\beta\nu,n}\ , \tag{4.14}$$

$$Q_{n,\beta\nu}=Q_{\beta\nu,n}\ , \tag{4.15}$$

$$P_{n,n}=E^{(n)}-E\ , \tag{4.16}$$

$$\langle v_\pm\rangle_{\mu\alpha}=\sum_{ab}C_a^*C_b\int d^3r\,u_\mu^\dagger[\delta_\alpha^\dagger V_{ab}]_\pm\ , \tag{4.17}$$

$$(v_{\pm})_n = \sum_{ab} C_a^{(n)*} C_b [V_{ab}]_{\pm} . \tag{4.18}$$

It is convenient to organize the linear equations [(4.6) to (4.9)] into a single matrix equation. For this purpose, we introduce a column vector Ξ,

$$\Xi = \begin{bmatrix} (X_{a\mu}) \\ (\xi_n) \\ (Y_{a\mu}) \\ (\eta_n) \end{bmatrix} , \tag{4.19}$$

a Hermitian matrix P,

$$P = \begin{bmatrix} (P_{a\mu,\beta\nu}) & (P_{a\mu,n}) \\ (P_{l,\beta\nu}) & (P_{l,n}) \end{bmatrix} , \tag{4.20}$$

and a symmetric matrix Q,

$$Q = \begin{bmatrix} (Q_{a\mu,\beta\nu}) & (Q_{a\mu,n}) \\ (Q_{l,\beta\nu}) & 0 \end{bmatrix} . \tag{4.21}$$

We arrange P and Q into a single Hermitian matrix

$$M = \begin{bmatrix} P & Q \\ Q^* & P^* \end{bmatrix} , \tag{4.22}$$

and introduce the diagonal matrix

$$\Omega = \begin{bmatrix} \Lambda & 0 \\ 0 & -\Lambda \end{bmatrix} , \tag{4.23}$$

where the diagonal submatrices Λ have the form

$$\Lambda = \begin{bmatrix} (\Lambda_a \delta_{a\beta} \delta_{\mu\nu}) & 0 \\ 0 & (\delta_{ln}) \end{bmatrix} . \tag{4.24}$$

We may then write Eqs. (4.6)–(4.9) as a single inhomogeneous equation

$$M\Xi = \omega\Omega\Xi - V , \tag{4.25}$$

where the vector V is given in terms of the external potential as

$$V = \begin{bmatrix} \langle v_+ \rangle_{\mu a} \\ (v_+)_n \\ -\langle v_- \rangle^*_{\mu a} \\ -(v_-)^*_n \end{bmatrix} . \tag{4.26}$$

In the absence of an external field, the inhomogeneous equation (4.25) reduces to an eigenvalue problem for the excitations of the atomic ground state:

$$M\Xi = \omega\Omega\Xi . \tag{4.27}$$

Any two solutions Ξ_k and Ξ_l of Eq. (4.27) belonging to distinct eigenvalues ω_k and ω_l are orthogonal with respect to the metric Ω. We normalize these solutions so that

$$\Xi_k^\dagger \Omega \Xi_l = \delta_{kl} . \tag{4.28}$$

The solution to the inhomogeneous equation (4.25) may be expanded in terms of eigenvectors of the homogeneous equation (4.27) as

$$\Xi = \sum_k \left[\frac{\Xi_k^\dagger \Omega V}{\omega - \omega_k} \right] \Xi_k . \tag{4.29}$$

The expansion (4.29) may be used to obtain a simple prescription for calculating transition amplitudes within the MCRRPA framework. The probability of a transition from the ground state to an excited state of the system induced by the time-dependent perturbation $V(t)$ of Eq. (1.2) is given by

$$|\langle n | v_+ | 0 \rangle|^2 = \operatorname*{Res}_{\omega = E_n - E_0} \langle \Psi(t) | v_+ e^{-i\omega t} | \Psi(t) \rangle_t , \tag{4.30}$$

where the subscript t on the right-hand side represents a time average, and where $\Psi(t)$ is the time-dependent state which evolves from the ground state in the presence of $V(t)$. In applying Eq. (4.30), only terms of second order in $v_{\pm}$ are retained after averaging over time. With this understanding, we find

$$\langle \Psi(t) | v_+ e^{-i\omega t} | \Psi(t) \rangle_t = \Xi^\dagger \Omega V . \tag{4.31}$$

Now by expanding Ξ in Eq. (4.31) in terms of eigenvectors of the homogeneous Eq. (4.27), we obtain

$$\langle \Psi(t) | v_+ e^{-i\omega t} | \Psi(t) \rangle_t = \sum_n \frac{|\Xi_n^\dagger \Omega V|^2}{\omega - \omega_n} . \tag{4.32}$$

The poles in Eq. (4.32) occur at the natural excitation frequencies of the atomic system. From (4.30) it follows that the transition probability from the ground state to the nth excited states is given by

$$|\langle n | v_+ | 0 \rangle|^2 = |\Xi_n^\dagger \Omega V|^2 . \tag{4.33}$$

The quantity $\Xi_n^\dagger \Omega V$ may therefore be interpreted as the MCRRPA amplitude for a transition from the ground state to the excited state having energy $E_n = E + \omega_n$.

Our approach to the MCRRPA equations is to solve the homogeneous differential equations written out in Sec. III directly, without using the matrix formulation explicitly. The matrix formulation, nevertheless, has the formal advantage of leading to convenient normalization conditions for the homogeneous orbitals $w_{\alpha\pm}$ and to explicit expressions for transition amplitudes from the ground state to each eigenstate of the homogeneous equations. In terms of orbitals, these expressions are

(i) Normalization condition:

$$\Xi_k^\dagger \Omega \Xi_k = \sum_{\alpha \le f} \Lambda_\alpha (\langle w_{\alpha+} \mid w_{\alpha+} \rangle - \langle w_{\alpha-} \mid w_{\alpha-} \rangle) + \sum_{a \le F} (\mid [C_a]_+ \mid^2 - \mid [C_a]_- \mid^2) = 1 \ . \tag{4.34}$$

(ii) Transition amplitude:

$$\Xi_k^\dagger \Omega V = \sum_{\alpha \le f} \Lambda_\alpha (\langle w_{a+} \mid v_+ \mid u_\alpha \rangle + \langle u_\alpha \mid v_- \mid w_{\alpha-} \rangle) + \sum_{a,b \le F} ([C_a]_+^* C_b + C_a^* [C_b]_-)(v_+)_{ab} \ . \tag{4.35}$$

In Eqs. (4.34) and (4.35) $w_{\alpha\pm}$ and $[C_a]_\pm$ are eigensolutions to the *homogeneous* MCRRPA equations of Sec. III corresponding to the eigenvalue ω_k.

V. ANGULAR DECOMPOSITION OF MCRRPA EQUATIONS

By assuming central-field forms for orbitals we can reduce the differential equations for the orbitals $(u_\alpha, w_{\alpha\pm})$ into radial forms and simplify the algebraic equations for weight coefficients $(C_a, [C_a]_\pm)$. These radial equations can then be solved self-consistently to give energies and wave functions for the ground state and its excitations. We write the orbitals in the form

$$u_\alpha(\vec{r}) = \frac{1}{r} \begin{bmatrix} G_{n_\alpha \kappa_\alpha} \Omega_{\kappa_\alpha m_\alpha} \\ i F_{n_\alpha \kappa_\alpha} \Omega_{-\kappa_\alpha m_\alpha} \end{bmatrix} \tag{5.1}$$

and introduce the two-component radial functions

$$u_\alpha \equiv u_\alpha(r) \equiv \begin{bmatrix} G_{n_\alpha \kappa_\alpha} \\ F_{n_\alpha \kappa_\alpha} \end{bmatrix} . \tag{5.2}$$

We also define the radial Hamiltonian operator, in atomic units, as

$$h_\alpha \equiv h_\alpha(r) = \begin{bmatrix} v_N(r) & -c\left[\frac{d}{dr} - \frac{\kappa_\alpha}{r}\right] \\ c\left[\frac{d}{dr} + \frac{\kappa_\alpha}{r}\right] & v_N(r) - 2c^2 \end{bmatrix} , \tag{5.3}$$

where $v_N(r)$ is the nuclear potential and c is the speed of light in atomic units, which equals the reciprocal of the fine-structure constant. Hence, we obtain the algebraic equation for C_a with $a \le F$:

$$\left[E - \sum_i [i]^2 (h_{ii} + \tfrac{1}{2} g_{ii}) - 2(h_{aa} + g_{aa})\right] C_a = \sum_{bl} (-)^l A_l(aabb;J) G_l(ab) C_b \ , \tag{5.4}$$

where

$$h_{\alpha\beta} = \int_0^\infty dr \, u_\alpha^\dagger(r) h_\beta(r) u_\beta(r) \ , \tag{5.5}$$

$$g_{\alpha\beta} = \sum_i [i]^2 \left[R_0(\alpha i;\beta i) - \sum_l D_l(\alpha i) R_l(\alpha i;i\beta)\right] , \tag{5.6}$$

$$R_l(\alpha\beta;\sigma\lambda) = \int_0^\infty dr_1 \int_0^\infty dr_2 u_\alpha^\dagger(r_1) u_\beta^\dagger(r_2) R_l(r_1 r_2) u_\sigma(r_1) u_\lambda(r_2) \ , \tag{5.7}$$

$$F_l(\alpha\beta) = R_l(\alpha\beta;\alpha\beta) \ , \tag{5.8}$$

$$G_l(\alpha\beta) = R_l(\alpha\beta;\beta\alpha) \ . \tag{5.9}$$

The angular coefficients in (5.4) and (5.6) are defined as

$$D_l(\alpha\beta) = \begin{bmatrix} \alpha & l & \beta \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{bmatrix}^2 \Pi(l_\alpha l l_\beta) \ , \tag{5.10}$$

with the parity function

$$\Pi(l_\alpha l l_\beta)=\begin{cases}1, & l_\alpha+l+l_\beta=\text{even},\\ 0, & l_\alpha+l+l_\beta=\text{odd},\end{cases} \tag{5.11}$$

and

$$A_l(\alpha\beta\sigma\lambda;J)=(-)^{J+l}C_l(\alpha\beta\sigma\lambda)\begin{Bmatrix}\alpha & \beta & J\\ \lambda & \sigma & l\end{Bmatrix}, \tag{5.12}$$

with

$$C_l(\alpha\beta\sigma\lambda)=(-)^{\alpha+\lambda}[\alpha\beta\sigma\lambda]\begin{pmatrix}\alpha & l & \sigma\\ \frac{1}{2} & 0 & -\frac{1}{2}\end{pmatrix}\begin{pmatrix}\beta & l & \lambda\\ \frac{1}{2} & 0 & -\frac{1}{2}\end{pmatrix}\Pi(l_\alpha l l_\sigma)\Pi(l_\beta l l_\lambda)\,. \tag{5.13}$$

In foregoing equations, we have used the abbreviations $\alpha\equiv j_\alpha$, etc. wherever the total angular momentum for a certain orbital is needed. The radial factor $R_l(r_1r_2)$ in (5.7) is

$$R_l(r_1r_2)=r_<^l/r_>^{l+1}\,. \tag{5.14}$$

We will choose the phase for the weight coefficients such that all C_a are real. The differential equations for u_α are then given by

(i) Core orbitals u_k :

$$\left[h_k-\epsilon_k+\sum_\alpha \Lambda_\alpha v_\alpha^{\mathrm{DF}}\right]u_k=-\sum_{\alpha\neq k}\lambda_{k\alpha}u_\alpha\,, \tag{5.15}$$

(ii) Valence orbitals u_a:

$$\left[h_a-\epsilon_a+\sum_i v_i^{\mathrm{DF}}\right]u_a=-\sum_b\frac{C_b}{C_a}[ab]\sum_l(-)^l D_l(ab)v_l(ab)u_b-\sum_{\alpha\neq a}\lambda_{a\alpha}u_\alpha\,. \tag{5.16}$$

Here we have defined

$$v_\alpha^{\mathrm{DF}}u_\beta=[\alpha]^2\left[v_0(\alpha\alpha)u_\beta-\sum_l D_l(\alpha\beta)v_l(\alpha\beta)u_\alpha\right], \tag{5.17}$$

and

$$v_l(\alpha\beta)=\int_0^\infty dr_2 u_\alpha^\dagger(r_2)R_l(r_1r_2)u_\beta(r_2)\,. \tag{5.18}$$

Equations (5.4) together with (5.15) and (5.16) are the usual MCDF equations expressed in radial form. To obtain radial MCRRPA equations, we follow the prescription [1]

$$w_{\alpha\pm}(\vec{r})=\sum_{\kappa_{\alpha'}m_{\alpha'}}(-)^{(M\mp M)/2}[J]\begin{pmatrix}j_{\alpha'} & m_\alpha & \pm M\\ m_{\alpha'} & j_\alpha & J\end{pmatrix}\times u_{\alpha'\pm}(\vec{r})\,\Pi(l_{\alpha'}l_\alpha J+\lambda-1)\,, \tag{5.19}$$

where

$$u_{\alpha'\pm}(\vec{r})=\frac{1}{r}\begin{pmatrix}G_{\alpha'\pm} & \Omega_{\kappa_{\alpha'}}m_{\alpha'}\\ iF_{\alpha'\pm} & \Omega_{-\kappa_{\alpha'}}m_{\alpha'}\end{pmatrix}. \tag{5.20}$$

The coupling coefficients in Eq. (5.19) are covariant 3-*jm* coefficients[13] and are chosen so that by replacing the orbital $u_\alpha(\vec{r})$ in the ground-state many-electron wave functions with the excitation $w_{\alpha\pm}(r)$ will result in a wave function with angular momentum J and M. The parameter λ in Eq. (5.19) determines the parity of the excited state JM; $\lambda=1$ corresponds to electric 2^J-pole excitations with parity $\pi=(-)^J$, while $\lambda=0$ corresponds to magnetic 2^J-pole excitations with parity $\pi=(-)^{J+1}$. We define the two-component radial functions by

$$u_{a'\pm}\equiv u_{a'\pm}(r)=\begin{bmatrix} G_{a'\pm} \\ F_{a'\pm} \end{bmatrix}. \tag{5.21}$$

By considering Eq. (5.19), we are led to assume for $[C_a]_\pm$ and $[\lambda_{\alpha\beta}]_\pm$ the forms

$$[C_a]_\pm=\delta_{JJ_a}\delta_{M\pm M_a}(-)^{(M\mp M)/2}C_{a\pm}\ , \tag{5.22}$$

$$[\lambda_{\alpha\beta}]_\pm=\sum_{\kappa_{\alpha'}m_{\alpha'}}(-)^{(M\mp M)/2}[J]\begin{pmatrix} j_{\alpha'} & m_\alpha & \pm M \\ m_{\alpha'} & j_\alpha & J \end{pmatrix}\lambda_{\alpha\pm\beta} \times\Pi(l_{\alpha'}l_\alpha J+\lambda-1)\ . \tag{5.23}$$

The angular decomposition of the MCRRPA equations can be performed after substituting (5.19), (5.22), and (5.23) into (3.42) and (3.43). This reduction can be accomplished most expediently using a graphical method.[13] The algebraic equations for $C_{a\pm}$ are obtained as

$$(E\pm\omega)C_{a\pm}=\sum_b[(H_{ab})_0C_{b\pm}+(H_{ab})_\pm C_b]\ , \tag{5.24}$$

where

$$(H_{ab})_0=\delta_{ab}\left[\sum_i[i][h_{ii}+\tfrac{1}{2}g_{ii}]+\sum_{\alpha=a_1,a_2}[h_{\alpha\alpha}+g_{\alpha\alpha}]\right] +\delta_{JJ_bN_aN_b}\sum_l[(-)^{l+b_1-b_2}A_l(a_1a_2b_1b_2;J)R_l(a_1a_2b_1b_2)+(-)^{J+l}A_l(a_1a_2b_2b_1;J)R_l(a_1a_2b_2b_1)]\ , \tag{5.25}$$

$$(H_{ab})_\pm=\frac{\sqrt{2}}{[b]}N_a\left\{(-)^{a_1+a_2}\left[\delta_{a_1b}(h_{a_2'\mp b}+g_{a_2'\mp b})+[b]^2\sum_l(-)^lD_l(a_1b)R_l(a_1a_2'\mp bb)\right]_{\kappa_{a_2'}=\kappa_{a_1}} -\delta_{a_1b}[(h_{a_2b'\pm}+g_{a_2b'\pm})_{\kappa_{a_2}=\kappa_{b'}}+f_{a_2b}] -\sum_{b'l}(-)^{J+l}A_l(a_1a_2b'b;J)R_l(a_1a_2b'\pm b)-(-)^{a_1+a_2-J}(1\leftrightarrow2)\right\}. \tag{5.26}$$

The notation $(1\leftrightarrow2)$ denotes all preceding terms inside the same brackets with the subscripts 1 and 2 interchanged. In (5.26), we have used the notation

$$f_{\alpha\beta}=\sum_{ii'}[(-)^{i-i'}T_J(\alpha i'\mp\beta i)+T_J(\alpha i\beta i'\pm)]\ , \tag{5.27}$$

with

$$T_J(\alpha\beta\sigma\lambda)=\frac{1}{[J]^2}C_J(\sigma\alpha)C_J(\beta\lambda)R_J(\alpha\beta\sigma\lambda)+(-)^{\beta+\lambda}\sum_l A_l(\sigma\alpha\beta\lambda;J)R_l(\alpha\beta\lambda\sigma)\ . \tag{5.28}$$

The differential equations for $u_{\alpha'\pm}$ are written for core and valence orbitals separately as

(i) Core excitation $u_{k'\pm}$:

$$\begin{aligned}&[h_{k'}-(\epsilon_k\pm\omega)+\sum_\alpha\Lambda_\alpha v_\alpha^{\mathrm{RPA}}]u_{k'\pm}\\ &=-\delta_{J0}\sum_{a\le F}C_a(C_{a+}+C_{a-})\frac{2[k]}{[a]^2}v_a^{\mathrm{DF}}u_k\\ &\quad+\sum_{\substack{a\le F\\ b>F}}N_b\frac{2}{[a]}C_a\{\delta_{ab_1}[C_{b\pm}w(b_1b_2)+(-)^{b_1-b_2}C_{b\mp}w(b_2b_1)]-(-)^{b_1+b_2-J}(1\leftrightarrow2)\}u_{k'\pm}\\ &\quad-\sum_{\alpha\ne k}\delta_{\kappa_k\kappa_\alpha}\delta_{\kappa_{k'}\kappa_{\alpha'}}\lambda_{k\alpha}u_{\alpha'\pm}-\sum_\alpha\delta_{\kappa_{k'}\kappa_\alpha}\lambda_{k\pm\alpha}u_\alpha\ ,\end{aligned} \tag{5.29}$$

where

$$w(\alpha\beta)u_{\lambda'\pm}=\frac{1}{[J]^2}C_J(\lambda\lambda')C_J(\alpha\beta)v_J(\alpha\beta)u_\lambda+(-)^{\alpha+\beta}\sum_l A_l(\lambda\lambda'\alpha\beta;J)v_l(\alpha\lambda)u_\beta\ , \tag{5.30}$$

$$v_\alpha^{\mathrm{RPA}}u_{\lambda'\pm}=v_\alpha^{\mathrm{DF}}u_{\lambda'\pm}+\sum_{\alpha'}[(-)^{\alpha-\alpha'}w(\alpha'\mp\alpha)+w(\alpha\alpha'\pm)]u_{\lambda'\pm}\ , \tag{5.31}$$

(ii) Valence excitation $u_{a'\pm}$:

$$\begin{aligned}\left[h_{a'\pm}-(\epsilon_a\pm\omega)+\sum_i v_i^{\mathrm{RPA}}\right]u_{a'\pm}&\\ =-\sum_{\substack{b\le F\\ l}}\frac{[a]}{[b]}\frac{C_b}{C_a}(-)^{J+l}&\Bigg\{[b]^2D_l(a'b)v_l(a'\mp b)u_b+\sum_{b'}A_l(aa'b'b;J)v_l(ab'\pm)u_b\\ &\qquad+\sum_{b'}(-)^{b-b'+J}A_l(aa'bb';J)v_l(ab)u_{b'\pm}\Bigg\}\\ +\delta_{J0}\sum_{b\le F}\frac{[a]^2}{C_a^2}&(C_{a\pm}C_b-C_aC_{b\pm})[b]\sum_l(-)^lD_l(ab)v_l(ab)u_b\\ +\sum_{d>F}N_d\frac{[a]}{\sqrt{2}C_a}C_{d\pm}&\Bigg\{\delta_{ad_1}\delta_{a'd_2}\sum_{b\le F}\frac{C_b}{C_{a'}}[a'b](-)^lD_l(a'b)v_l(d_2b)u_b\\ &\qquad+\sum_l(-)^{d_1+d_2+l}A_l(aa'd_1d_2;J)v_l(ad_1)u_{d_2}-(-)^{d_1+d_2-J}(1\leftrightarrow2)\Bigg\}\\ -\sum_{\alpha\ne a}\delta_{\kappa_a\kappa_\alpha}\delta_{\kappa_{a'}\kappa_{\alpha'}}&\lambda_{a\alpha}u_{\alpha'\pm}-\sum_\alpha\delta_{\kappa_{a'}\kappa_\alpha}\lambda_{a\pm\alpha}u_\alpha\ ,\end{aligned} \tag{5.32}$$

where $a'\le F$, and where $u_{a'}$ and $u_{a'\pm}$ have the same angular symmetry. Equations (5.24), (5.29), and (5.32) constitute an eigenvalue problem for the radial components of the perturbed orbitals $u_{a'\pm}$ and for the perturbed weight coefficients $C_{a\pm}$. The solutions to these equations describe the excited states of the atom having a given angular momentum and parity $J,\Pi=(-1)^{J+\lambda-1}$. These eigenstates are normalized according to the rule (4.34) which may be written in terms of radial functions as

$$\sum_{\alpha\alpha'}\Lambda_\alpha[(u_{\alpha'+},u_{\alpha'+})-(u_{\alpha'-},u_{\alpha'-})]+\sum_{a\le F}[\,|C_{a+}|^2-|C_{a-}|^2]=1\ . \tag{5.33}$$

Let us assume that the perturbing field is a sum of electric and magnetic multipole terms $v_{JM}^{(\lambda)}$:

$$v_+=\sum_{JM\lambda}v_{JM}^{(\lambda)}\ . \tag{5.34}$$

A given term in (5.34) will lead to a spectrum of excited states having the same angular momentum and parity as the perturbation. The transition amplitude from the ground state to one such state is given from (4.35) as

$$T_J^{(\lambda)}=\sum_\alpha\Lambda_\alpha(\langle w_{\alpha+}\,|\,v_{JM}^{(\lambda)}\,|\,u_\alpha\rangle+\langle u_\alpha\,|\,v_{JM}^{(\lambda)}\,|\,w_{\alpha-}\rangle)+\sum_{ab}([C_a]_+^*C_b+C_a^*[C_b]_-)(v_{JM}^{(\lambda)})_{ab}\ . \tag{5.35}$$

Let us define the interaction strength $X_J^{(\lambda)}(\alpha\beta)$ to be the reduced matrix element of the irreducible tensor $v_{JM}^{(\lambda)}$ between orbitals α and β[13]

$$\langle\alpha\,|\,v_{JM}^{(\lambda)}\,|\,\beta\rangle=\begin{pmatrix}\alpha & M & m_\beta\\ m_\alpha & J & \beta\end{pmatrix}X_J^{(\lambda)}(\alpha\beta)\ . \tag{5.36}$$

The MCRRPA transition amplitude $T_J^{(\lambda)}$ can be written in terms of the interaction strength $X_J^{(\lambda)}(\alpha\beta)$ using (5.19), (5.22), and (5.36):

$$T_J^{(\lambda)}=\frac{1}{[J]}(-)^{J+1}\sum_{\alpha\alpha'}\Lambda_\alpha[(-)^\lambda X_j^{(\lambda)}(\alpha\alpha'+)+X_J^{(\lambda)}(\alpha\alpha'-)]$$
$$+\frac{1}{[J]}(-)^J\sum_{\substack{a\le F\\ b>F}}\frac{\sqrt{2}}{[a]}C_a[(-)^\lambda C_{b+}+C_{b-}][\delta_{ab_1}+(-)^{J+\lambda}\delta_{ab_2}]X_J^{(\lambda)}(b_1b_2)\,. \tag{5.37}$$

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