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# Multichannel relativistic random-phase approximation for the photoionization of atoms

W. R. Johnson
*Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556*

C. D. Lin
*Department of Physics, Kansas State University, Manhattan, Kansas 66506*
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A multichannel relativistic random-pjase approximation (RRPA) for the photoionization of atoms is presented. The RRPA equations are obtained by generalizing the nonrelativistic time-dependent Hartree-Fock equations using the Dirac-Breit Hamiltonian to describe the atomic electrons. The angular decomposition of the RRPA equations to a set of coupled equations for the radial wave functions is given, and the radiative-transition operators are developed for arbitrary electric and magnetic multipoles. Formulas are obtained for the total photoionization cross sections and angular distributions, including all multipoles. The method of constructing multichannel solutions from the RRPA radial wave functions is described and various ways of choosing approximate potentials for the photoelectron are given.

## I. INTRODUCTION

Experimental and theoretical studies of atomic photoionization have greatly increased our understanding of the role of electron correlation in radiative processes.[1,2] By comparing experimental photoionization cross sections with the results of the independent electron approximation, one finds that many-electron effects, typically the interaction of the escaping electron with the residual ion, are important; especially for photoelectrons at low energies. Various theoretical techniques have been employed to study many-electron correlation effects in atoms; among the simplest and most widely applied of these techniques is the random-phase approximation (RPA).[1,3] By treating certain types of correlation to all orders (in the sense of perturbation theory) the analysis of photoexcitation or photoionization can be reduced to the solution of a set of integrodifferential equations (the RPA equations) similar in structure to the familiar Hartree-Fock equations.[4] Extensive comparisons of nonrelativistic RPA predictions with experiment lead to the conclusion that the RPA includes most of the important correlation effects for photoionization processes.[1]

With the increasing availability of synchroton radiation as a light source, and with the rapid advance of photoelectron spectroscopy, many precision measurements of atomic photoionization are becoming available. In these experiments not only cross sections from individual subshells but also photoelectron angular distributions are determined. These cross sections and angular distributions contain complementary information; the cross sections depend on the size of the transition amplitudes, while the angular distributions are sensitive to relative phases.

One deficiency of the RPA is the omission of relativistic effects, such as the spin-orbit interaction. These effects are generally thought to be small, but they show up in precision measurements, often in striking ways. A well-known example of relativistic effects is the $4d_{5/2}$:$4d_{3/2}$ cross section ratio in Xe.[5] If the relativistic effects were omitted, this ratio would be 3:2 independent of energy; whereas experiment shows a rapid variation of the branching ratio with energy in harmony with relativistic calculations.[6] Another example of relativistic effects is the asymmetry parameter $\beta$ for the angular distribution of $5s_{1/2}$ electrons in Xe. According to the nonrelativistic theory, the value of $\beta$ is 2, independent of energy, while experiment and relativistic theory[7] both show significant deviation from the nonrelativistic value, particularly at an energy where the cross section is near the "Cooper minimum."

Relativistic theory has been applied previously to study photoionization above 1 keV,[8,9] where the inner-shell contributions dominate the cross section. It has also been applied to study the photoionization of outer shells in heavy atoms at low energies.[10] In these studies correlation is omitted and the photoelectron is assumed to move in a local potential (often taken to be a Dirac-Fock potential with exchange treated statistically). More recently relativistic calculations have appeared in which the outer shells of heavy atoms are studied using a Dirac-Fock potential equivalent to the $V_{jj}^{(N-1)}$ potential discussed later in this paper.[11]

Experience with the nonrelativistic theory leads to the conclusion that at low photon energies where outer shells contribute most significantly to the

 

photoionization the effects of correlation are important (usually much more important than relativistic effects). It is desirable that the introduction of relativistic effects into the theory should be accompanied by a parallel consideration of correlation. With the success of the RPA and its simplicity, we are led to consider the relativistic random phase approximation (RRPA) as a method to study relativistic effects in photoionization, particularly in situations where correlations are expected to be important.

In this paper we present a complete description of the multichannel RRPA theory for the photoionization of atoms. This relativistic theory is derived in Sec. II using a generalization of the time-dependent Hartree-Fock method. After explaining how these RRPA equations are reduced to a system of coupled radial equations, we describe, in Sec. III, the partial wave decomposition of the multipole transition amplitudes. A prescription for solving the multichannel RRPA equations is given in Sec. IV. The question of choosing different gauges for the electric multipole transitions and the different ways of choosing approximate potentials for the photoelectrons are also discussed at some length.

## II. RRPA EQUATIONS

### A. Time-dependent Hartree-Fock theory

The RRPA theory is most conveniently obtained by linearizing the time-dependent Hartree-Fock (TDHF) equations[12] describing the response of an atom to a time-dependent external field. Let us represent the ground state of an $N$-electron closed-shell atom using a single Slater determinant of $N$ Dirac-Fock (DF) orbitals $u_i(\vec{r})$. These orbitals satisfy the DF equations:

$$(h_0+V)u_i=\epsilon_i u_i\,,\quad i=1,2,\ldots,N \tag{1}$$

where $h_0=\vec{\alpha}\cdot\vec{p}+\beta m-Ze^2/r$ is a single-electron Dirac Hamiltonian and where $\epsilon_i$ is an orbital eigenvalue. In Eq. (1) and throughout the remainder of the text, we employ natural units: $\hbar=c=1$. The DF potential $V(r)$ in Eq. (1) is given by

$$Vu(\vec{r})=\sum_{j=1}^{N}e^2\int\frac{d^3r'}{|\vec{r}-\vec{r}'|}[(u_j^\dagger u_j)'u-(u_j^\dagger u)'u_j]\,. \tag{2}$$

Application of a time-dependent external field $v_+e^{-i\omega t}+v_-e^{i\omega t}$ induces a time-dependent perturbation in each of the DF orbitals $u_i(\vec{r})$; thus,

$$u_i(\vec{r})\to u_i(\vec{r})+w_{i+}(\vec{r})e^{-i\omega t}+w_{i-}(\vec{r})e^{i\omega t}+\cdots\,, \tag{3}$$

where the omitted terms are the higher harmonics. The generalization of the DF equations (1) to such a time-dependent situation when all the higher harmonics are included leads to a relativistic version of the nonlinear TDHF equations. If, following Dalgarno and Victor,[4] we expand the TDHF equations in powers of the external field and retain only first-order terms, a set of linearized TDHF equations for the orbitals $w_{i\pm}(\vec{r})$ are obtained:

$$(h_0+V-\epsilon_i\mp\omega)w_{i\pm}=(v_\pm-V_\pm^{(1)})u_i+\sum_j\lambda_{ij\pm}u_j\,,$$
$$i=1,2,\ldots,N. \tag{4}$$

In Eq. (4) $V$ is the DF potential and

$$V_\pm^{(1)}u_i(\vec{r})=\sum_{j=1}^{N}e^2\int\frac{d^3r'}{|\vec{r}-\vec{r}'|}[(u_j^\dagger w_{j\pm})'u_i+(w_{j\mp}^\dagger u_j)'u_i-(w_{j\mp}^\dagger u_i)'u_j-(u_j^\dagger u_i)'w_{j\pm}]\,. \tag{5}$$

includes the electron-electron correlation. The Lagrange multipliers $\lambda_{ij\pm}$ are introduced in Eq. (4) to insure the orthogonality of the perturbed orbitals $w_{i\pm}(\vec{r})$ to the occupied orbitals $u_i(\vec{r})$.

The fundamental RRPA equations are obtained by omitting the "driving" terms $v_\pm$ from Eqs. (4), leading to the eigenvalue problem

$$\pm(h_0+V-\epsilon_i)w_{i\pm}\pm V_\pm^{(1)}u_i\mp\sum_j\lambda_{ij\pm}u_j=\omega w_{i\pm}\,,$$
$$i=1,2,3,\ldots,N. \tag{6}$$

It is natural to study this eigenvalue problem since any solution to the inhomogeneous equation (4) can be expanded in terms of eigenfunctions of Eq. (6). The eigenvalues of Eq. (6) provide an approximation to the excitation spectrum of the atom, including the discrete range as well as a continuum. The positive frequency components of the eigenfunctions, $w_{i+}$, provide a description of the excited states of the atom including final-state correlations, while the negative frequency components $w_{i-}$ describe the effects of correlations in the ground state.[3] The perturbed orbitals $w_{i\pm}$ are coupled together through the first-order potential $V_\pm^{(1)}$. The eigenfunctions $w_{j\pm}$ are subject to the orthogonality constraint

$$\int d^3r\; w_{i\pm}^\dagger u_j=0\,,\quad i,j=1,2,\ldots,N. \tag{7}$$

Normalization of the orbitals in Eq. (6) is chosen so that for two excitation energies $\omega_A$ and $\omega_B$ the corresponding eigenfunctions $w_{i\pm}^A$ and $w_{i\pm}^B$ satisfy

$$\sum_{i=1}^{N}\int d^3r(w_{i+}^{\dagger A}w_{i+}^B-w_{i-}^{\dagger A}w_{i-}^B)=\delta(\omega_A,\omega_B)\,. \tag{8}$$

For continuum orbitals, this corresponds to the normalization on the energy scale.

As mentioned above, any solution to Eq. (4) can be expanded in terms of a complete set of solu-

tions to the homogeneous equations (6). Using this fact the amplitude for a transition from the ground state to the excited state described by the RRPA function $w_{i\pm}(\vec{r})$ of frequency $\omega$, induced by $v_+e^{-i\omega t}+v_-e^{i\omega t}$ is found to be

$$T=\sum_{i=1}^{N}\int d^3r\,(w_{i+}^{\dagger}v_+u_i+w_{i-}^{\dagger}v_-u_i)\,. \tag{9}$$

For an electromagnetic interaction, the perturbations $v_\pm$ are described in the Coulomb gauge in terms of the vector potential $\vec{A}$ by

$$v_+=e\vec{\alpha}\cdot\vec{A}\,,\quad v_-=v_+^{\dagger}\,. \tag{10}$$

Other gauges lead to similar expressions as will be discussed later. Thus, for an electromagnetic transition, the RRPA amplitude is given by

$$T=\sum_{i=1}^{N}e\int d^3r\,(w_{i+}^{\dagger}\vec{\alpha}\cdot\vec{A}u_i+u_i^{\dagger}\vec{\alpha}\cdot\vec{A}w_{i-})\,. \tag{11}$$

### B. Angular decomposition

#### 1. *Radial Dirac-Fock equations*

The DF orbitals $u(\vec{r})$ in Eq. (1) are expressed in terms of spherical spinors $\Omega_{\kappa m}(\hat{r})$ and radial functions $G_{n\kappa}(r)$ for the large component, and $F_{n\kappa}(r)$ for the small component;

$$u(\vec{r})=\frac{1}{r}\begin{pmatrix} iG_{n\kappa}(r) & \Omega_{\kappa m}(\hat{r})\\ F_{n\kappa}(r) & \Omega_{-\kappa m}(\hat{r})\end{pmatrix}. \tag{12}$$

The subscripts $n$, $\kappa$, and $m$ are principal and angular momentum quantum numbers; $\kappa=\mp(j+\frac{1}{2})$ for $j=l\pm\frac{1}{2}$, where $j$ and $l$ are the total and orbital angular momenta of the electron. As usual, $m$ is the $z$ component of the total angular momentum. The spherical spinor $\Omega_{\kappa m}(\hat{r})$ is given in terms of spherical harmonics $Y_{lm_l}(\hat{r})$ and two-component Pauli spinors $\chi_\lambda$ as

$$\Omega_{\kappa m}(\hat{r})=\sum_{\lambda}\langle lm-\lambda\tfrac{1}{2}\lambda|l\tfrac{1}{2}jm\rangle\,Y_{lm-\lambda}(\hat{r})\chi_\lambda\,. \tag{13}$$

Various phase conventions are adopted for the decomposition in Eq. (12). We adhere to the convention given in Akhiezer and Berestetskii.[13] Since the phase conventions are not uniform, some care must be exercised in comparing the radial equations written down by various authors.

For a closed-shell atom the DF equations reduce to a simple form. Let us introduce the two-component radial functions:

$$\mathcal{F}_{n\kappa}(r)=\begin{pmatrix} G_{n\kappa}(r)\\ F_{n\kappa}(r)\end{pmatrix}. \tag{14}$$

Each of the radial functions for the electrons in a given subshell are of course identical. We use a single Latin subscript $a,b,\ldots$ to designate the pair $(n,\kappa)$. The DF potential $V$ of Eq. (2) may be expressed in terms of radial functions as:

$$V\mathcal{F}_a(r)=\sum_b(2j_b+1)\left(e^2\frac{Y_0(b,b,r)}{r}\mathcal{F}_a(r)-\sum_l\Lambda_l(a,b)\times e^2\frac{Y_l(b,a,r)}{r}\mathcal{F}_b(r)\right). \tag{15}$$

The subscript $b$ ranges over all of the distinct atomic subshells and $l$ is an integer limited by the selection rules in the angular factor $\Lambda_l(a,b)$ defined below. The Hartree screening function $Y_l(a,b,r)$ in Eq. (15) is given by

$$Y_l(a,b,r)=\frac{1}{r^l}\int_0^r r^l\mathcal{F}_a^{\dagger}\mathcal{F}_b\,dr+r^{l+1}\int_r^{\infty}\frac{dr}{r^{l+1}}\mathcal{F}_a^{\dagger}\mathcal{F}_b\,. \tag{16}$$

The angular factor $\Lambda_l(a,b)$ is defined as

$$\Lambda_l(a,b)=\begin{pmatrix} j_a & j_b & l\\ -\frac{1}{2} & \frac{1}{2} & 0\end{pmatrix}^2\pi(l_a,l_b,l)\,, \tag{17}$$

where the large round bracket designates a $3$-$j$ symbol and where $\pi$ is a parity factor

$$\pi(l_a,l_b,l)=\begin{cases}1\,, & l_a+l_b+l=\text{even}\\ 0\,, & l_a+l_b+l=\text{odd}\,.\end{cases} \tag{18}$$

If we introduce the radial Hamiltonian operator

$$H_a=\begin{bmatrix} m-\frac{Ze^2}{r}+V & \left(\frac{d}{dr}-\frac{\kappa_a}{r}\right)\\ -\left(\frac{d}{dr}+\frac{\kappa_a}{r}\right) & -m-\frac{Ze^2}{r}+V\end{bmatrix}, \tag{19}$$

we may then write the DF equations as

$$(H_a-\epsilon_a)\mathcal{F}_a=0\,, \tag{20}$$

where $a$ ranges over distinct closed subshells.[14]

#### 2. *Radial RRPA equations*

Let us consider a particular unperturbed DF orbital $u_{n\kappa m}(\vec{r})$ and construct the corresponding perturbed orbitals $w_{n\kappa m\pm}(\vec{r})$ describing an atomic excited state of angular momentum $(J,M)$ and parity $\pi$. The ion formed by removing orbital $u_{n\kappa m}$ will have angular momentum $(J_I,M_I)=(j,-m)$ and parity $\pi_I=(-1)^l$. We decompose $w_{n\kappa m}(\vec{r})$ into angular momentum components $\bar{j}$, $\bar{l},\bar{m}$, weighted so that the excited electron-ion combinations will give the required atomic state $J,M,\pi$. The parity of the atom will be $(-1)^{l+\bar{l}}$,

so that states excited by electric (magnetic) $2^J$-pole radiation must have $l+\bar{l}+J=$ even(odd). To obtain the required atomic state we write

$$w_{n\kappa m+}(\vec{r}) = \sum_{\bar{\kappa}\bar{m}} (-1)^{j-m}\langle j\,-m\,\bar{j}\,\bar{m}\,|\,j\,\bar{j}\,JM\rangle \times \pi(l,\bar{l},J+\lambda-1)\,y_{(n\kappa)\bar{\kappa}\bar{m}+}(\vec{r})\,, \tag{21a}$$

$$w_{n\kappa m-}(\vec{r}) = \sum_{\bar{\kappa}\bar{m}} (-1)^{j-m+M}\langle j\,-m\,\bar{j}\,\bar{m}\,|\,j\,\bar{j}\,J\,-M\rangle \times \pi(l,\bar{l},J+\lambda-1)\,y_{(n\kappa)\bar{\kappa}\bar{m}-}(\vec{r})\,. \tag{21b}$$

The coupling coefficients in Eq. (21a) are chosen so that replacing the orbital $u_{n\kappa m}(\vec{r})$ in the ground-state many-electron wave function by the excited-state orbital $w_{n\kappa m}(\vec{r})$ will result in an excited-state wave function with angular momentum $J$ and $M$. The phase differences between Eqs. (21a) and (21b) are needed in order to separate the RRPA Eqs. (6) into radial components. The parameter $\lambda$ in Eqs. (21) determines the parity of the excited state $J,M$; $\lambda=1$ corresponds to electric $2^J$-pole excitations with parity $\pi=(-1)^J$, while $\lambda=0$ corresponds to magnetic excitations with parity $\pi=(-1)^{J+1}$. The angular momentum components $y_{(n\kappa)\bar{\kappa}\bar{m}\pm}$ represent perturbations from definite orbitals $n\kappa$ into distinct angular momentum states $\bar{\kappa}$. We write

$$y_{(n\kappa)\bar{\kappa}\bar{m}\pm}(\vec{r}) = \frac{1}{r}\begin{pmatrix} iS_{(n\kappa)\bar{\kappa}\pm}(r) & \Omega_{\bar{\kappa}\bar{m}}(\hat{r}) \\ T_{(n\kappa)\bar{\kappa}\pm}(r) & \Omega_{-\bar{\kappa}\bar{m}}(\hat{r}) \end{pmatrix}. \tag{22}$$

To make our notation somewhat more compact let us designate the quantum numbers $(n\kappa)$ of the unperturbed orbital by the letter $a=(n\kappa)$ as before and designate the specific excitation $(n\kappa)\to\bar{\kappa}$ by the letter $\bar{a}$. We may then collect the large and small component radial functions into a two-component vector

$$y_{\bar{a}\pm}(r) = \begin{pmatrix} S_{\bar{a}\pm}(r) \\ T_{\bar{a}\pm}(r) \end{pmatrix}. \tag{23}$$

For convenience we introduce two auxiliary angular functions

$$C_J(a,b) = (-1)^{j_a+1/2}[j_a][j_b]\begin{pmatrix} j_a & j_b & J \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}\pi(l_a,l_b,J) \tag{24a}$$

and

$$A(a,b,c,d,l,J) = (-1)^{l+J-j_c-j_b}C_l(a,b)C_l(c,d) \times \begin{Bmatrix} j_a & j_b & l \\ j_d & j_c & J \end{Bmatrix}\pi(l_a,l_c,J)\pi(l_b,l_d,J)\,, \tag{24b}$$

where $[j]=(2j+1)^{1/2}$, and where the large curly bracket is a 6-$j$ symbol. Later we will use the shorthand notation $a\to -a$ in Eq. (24) to represent the replacement $\kappa_a\to-\kappa_a$, which modifies the parity selection rules only.

To reduce the RRPA equations to radial forms, let the radial Hamiltonian $H_a$ be defined just as in Eq. (19) with $V$ as the unperturbed DF potential given in Eq. (15). The first two terms in Eq. (5) can be collected together in a potential:

$$V_J^{(1)}(r) = \sum_{b,\bar{b}} \frac{C_J(b,\bar{b})}{[J]^2}\left(\frac{e^2}{r}\,Y_J(b,\bar{b}+,r) + \frac{e^2}{r}\,Y_J(b,\bar{b}-,r)\right), \tag{25}$$

where the sum ranges over all of the perturbations $\bar{b}$ of all of the subshells $b$ of the atom. The symbols $\bar{b}+$ and $\bar{b}-$ in the Hartree screening functions $Y_J$ refer to the radial functions $y_{\bar{b}\pm}(r)$ of Eq. (23), while $b$ refers to the functions $\mathfrak{F}_b(r)$ of Eq. (14). From the RRPA equations (6), we then find:

(i) *"Electric" case;* $J^\pi, \pi=(-1)^J$

$$[H_{\bar{a}}-(\epsilon_a\pm\omega)]y_{\bar{a}\pm} = -C_J(a,\bar{a})V_J^{(1)}(r)\mathfrak{F}_a + \sum_{b,\bar{b},l}\left(A(a,b,\bar{a},\bar{b},l,J)\frac{e^2}{r}\,Y_l(a,b,r)y_{\bar{b}\pm} + (-1)^{j_b-j_{\bar{b}}}A(a,\bar{b},\bar{a},b,l,J)\frac{e^2}{r}\,Y_l(a,\bar{b}\mp,r)\mathfrak{F}_b\right) + \sum_b \delta_{\kappa_b\bar{\kappa}_a}\lambda_{\bar{a}b\pm}\mathfrak{F}_b \tag{26}$$

(ii) *"Magnetic" case;* $J^\pi, \pi=(-1)^{J+1}$

$$[H_{\bar{a}}-(\epsilon_a\pm\omega)]y_{\bar{a}\pm} = \sum_{b,\bar{b},l}\left(A(-a,-b,\bar{a},\bar{b},l,J)\frac{e^2}{r}\,Y_l(a,b,r)y_{\bar{b}\pm} + (-1)^{j_b-j_{\bar{b}}}A(-a,-\bar{b},\bar{a},b,l,J)\frac{e^2}{r}\,Y_l(a,\bar{b}\mp,r)\mathfrak{F}_b\right) + \sum_b \delta_{\kappa_b\bar{\kappa}_a}\lambda_{\bar{a}b\pm}\mathfrak{F}_b\,. \tag{27}$$

The "electric" equations (26) with $J=1$ describe the excited atomic states associated with low energy photoionization and will be considered in greater detail later in this paper. The "electric" equations for $J \geq 2$ and the "magnetic" equations for $J \geq 1$ describe atomic states excited from the atomic ground state by higher-order multipole radiation; only limited applications of these higher-order RRPA equations have been made in the past.[15] We call attention to the absence of the direct first-order potential $V_J^{(1)}$ in the "magnetic" case and to the replacements $a \rightarrow -a, b \rightarrow -b$, associated with the parity selection rules. The similarity between the radial RRPA equations (26) and (27) and the radial DF equations (20) should be noted; the only significant difference is the appearance of terms on the right of Eqs. (26) and (27) coupling the perturbed orbitals.

To satisfy the orthogonality requirement (7), we choose the Lagrange multipliers $\lambda_{\bar{a}b\pm}$ so that the perturbed radial functions $y_{\bar{a}\pm}$ are orthogonal to the unperturbed orbitals having the same angular symmetry:

$$\int_0^\infty dr\, y_{\bar{a}\pm}^\dagger \mathcal{F}_b = 0\,, \quad \text{for } \bar{\kappa}_a = \kappa_b\,. \tag{28}$$

The normalization condition of Eq. (8) becomes

$$\sum_{a,\bar{a}} \int_0^\infty dr\,(y_{\bar{a}+}^{A\dagger} y_{\bar{a}+}^{B} - y_{\bar{a}-}^{A\dagger} y_{\bar{a}-}^{B}) = \delta(\omega_A, \omega_B) \tag{29}$$

for perturbed orbitals with a given angular symmetry $J^\pi$ having energies $\omega_A$ and $\omega_B$.

## III. ATOMIC PHOTOIONIZATION USING RRPA

### A. Gauges and multipole transition amplitudes

A photon with wave vector $\vec{k}$, frequency $\omega$, and polarization vector $\hat{\epsilon}$ excites a closed-shell atom from its $^1S_0$ ground state to a continuum state consisting of an electron moving off with momentum $\vec{p}$, energy $E$, and a residual ion. We write the photon vector potential (in the Coulomb gauge) as

$$\vec{A} = \hat{\epsilon} e^{i\vec{k}\cdot\vec{r}}\,. \tag{30}$$

For convenience we decompose the vector potential into multipole components. We write

$$\vec{A} = 4\pi \sum_{JM\lambda} i^{J-\lambda} [\vec{Y}_{JM}^{(\lambda)}(\hat{k}) \cdot \hat{\epsilon}] \vec{a}_{JM}^{(\lambda)}(\vec{r})\,. \tag{31}$$

The indices $J$ and $M$ are photon angular momentum quantum numbers and $\lambda = 1$ or 0 for electric or magnetic multipoles, respectively. The vector spherical harmonics $\vec{Y}_{JM}^{(\lambda)}(\hat{k})$ are defined in Ref. 13. In the Coulomb gauge we may write the multipole components $\vec{a}_{JM}^{\lambda}(\vec{r})$ as:

*1. Coulomb gauge*

$$\vec{a}_{JM}^{(0)} = j_J(\omega r)\vec{Y}_{JM}^{(0)}\,, \tag{32a}$$

$$\vec{a}_{JM}^{(1)} = [j_J'(\omega r) + j_J(\omega r)/\omega r]\vec{Y}_{JM}^{(1)} + [J(J+1)]^{1/2} j_J(\omega r)/\omega r\, \vec{Y}_{JM}^{(-1)}\,, \tag{32b}$$

where $j_J(\omega r)$ is a spherical Bessel function and where $j_J'(\omega r)$ is the derivative with respect to its argument. Dipole matrix elements ($J=\lambda=1$) evaluated using the Coulomb gauge potentials reduce, in the nonrelativistic limit, to matrix elements of the velocity operator.

If, instead of the Coulomb gauge vector potential $\vec{A}$, we introduce potentials $\vec{A}'$ and $\phi'$ obtained from $\vec{A}$ by a gauge transformation

$$\vec{A}' = \vec{A} + \vec{\nabla}\chi\,, \qquad \phi' = i\omega\chi\,, \tag{33}$$

then the interaction $v_+$ in Eq. (10) is replaced by

$$v_+' = v_+ + e(\vec{\alpha}\cdot\vec{\nabla}\chi - i\omega\chi)\,. \tag{34}$$

The modification $v_+ \rightarrow v_+'$ leads to a corresponding change in the transition amplitude in Eq. (11), viz.,

$$T \rightarrow T' = T + \sum_i e \int d^3r' [w_{i+}^\dagger(\vec{\alpha}\cdot\vec{\nabla}\chi - i\omega\chi)u_i + u_i^\dagger(\vec{\alpha}\cdot\vec{\nabla}\chi - i\omega\chi)w_{i-}]\,. \tag{35}$$

The sum on the right-hand side of Eq. (35) may be evaluated with the aid of the RRPA equations (6) and shown to vanish.[16] Thus we are led to the gauge independence property of the RRPA:

$$T' = T\,. \tag{36}$$

It should be remarked that the transition amplitude is also gauge independent in a potential theory, while other theories, such as multiconfiguration Hartree-Fock theory, give gauge dependent amplitudes.[17] In some practical applications we truncate the RRPA equations to simplify the numerical calculations. The sum on the right in Eq. (35) does *not* cancel in such truncated RRPA calculations; however, we may use the size of the residual difference to measure the error associated with the truncation.

Under a gauge transformation the multipole potentials become

$$\vec{a}_{JM}^{(\lambda)\prime} = \vec{a}_{JM}^{(\lambda)} + \vec{\nabla}\chi_{JM}\,, \qquad \phi_{JM}' = i\omega\chi_{JM}\,, \tag{37}$$

where $\chi_{JM}$ is the gauge function. One particularly useful choice of $\chi_{JM}$ leads to dipole matrix elements which reduce to matrix elements of the length operator nonrelativistically; we call this the length gauge[17]:

*2. Length gauge*

$$\vec{a}^{(0)'}_{JM} = j_J(\omega r)\vec{Y}^{(0)}_{JM}, \tag{38a}$$

$$\vec{a}^{(1)'}_{JM} = -j_{J+1}(\omega r)\{\vec{Y}^{(1)}_{JM} - [(J+1)/J]^{1/2}\vec{Y}^{(-1)}_{JM}\}, \tag{38b}$$

$$\phi'_{JM} = -i[(J+1)/J]^{1/2} j_J(\omega r) Y_{JM}(\hat{r}). \tag{38c}$$

The multipole transition amplitude is given in terms of the multipole fields, from Eq. (11) as

$$T^{(\lambda)}_{JM} = \sum_j \int d^3r\, (w^\dagger_{j+}\vec{\alpha}\cdot\vec{a}^{(\lambda)}_{JM}u_j + u^\dagger_j\vec{\alpha}\cdot\vec{a}^{(\lambda)}_{JM}w_{j-}) \tag{39}$$

in the Coulomb gauge, or by Eq. (39) with

$$\vec{\alpha}\cdot\vec{a}^{(\lambda)}_{JM} \to \vec{\alpha}\cdot\vec{a}^{(\lambda)'}_{JM} - \phi'_{JM}$$

in the length gauge. The only nonvanishing contributions to $T^{(\lambda)}_{JM}$ come from electric or magnetic multipole solutions to the RRPA equations with exactly the same "multipolarity" $JM\lambda$ as the potential $\vec{a}^{(\lambda)}_{JM}$.

### B. Partial-wave decomposition of transition amplitudes

One simple way to describe the analysis of the multi-electron amplitude $T$ of Eq. (39) is by reference to the corresponding single-electron theory in which an electron [described by $u_i(\vec{r})$] moving in a central potential $V(r)$ makes a transition to a continuum state [described by $w_i(\vec{r})$]. The final-state orbital $u_i(\vec{r})$, which must satisfy "incoming" wave boundary conditions, is expanded in partial waves as

$$w_i(\vec{r}) = \left(\frac{(2\pi)^3}{Ep}\right)^{1/2}\sum_{\bar{\kappa}m}(\Omega^\dagger_{\bar{\kappa}m}(\hat{p})\chi_\nu)i^{\bar{l}-1}e^{-i\delta_{\bar{\kappa}}} \times\frac{1}{r}\begin{pmatrix} iS_{\bar{\kappa}}(r)\Omega_{\bar{\kappa}m} \\ T_{\bar{\kappa}}(r)\Omega_{-\bar{\kappa}m}\end{pmatrix}, \tag{40}$$

where $\vec{p}$ is the momentum, $E$ the energy, $\nu$ the spin projection, and $\delta_{\bar{\kappa}}$ the partial-wave phase shift. The large and small component functions $S_{\bar{\kappa}}(r)$ and $T_{\bar{\kappa}}(r)$ satisfy radial Dirac equations in an effective potential $V(r)$. We collect together $S_{\bar{\kappa}}(r)$ and $T_{\bar{\kappa}}(r)$ in a two-component radial function

$$y_{\bar{\kappa}}(r) = \begin{pmatrix} S_{\bar{\kappa}}(r) \\ T_{\bar{\kappa}}(r)\end{pmatrix}. \tag{41}$$

This radial function, normalized on the energy scale, behaves asymptotically as

$$y_{\bar{\kappa}}(r) \xrightarrow[r\to\infty]{} \begin{pmatrix} \left(\frac{E+m}{\pi p}\right)^{1/2}\cos[pr + \nu\ln(2pr) - \tfrac{1}{2}(\bar{l}+1)\pi + \delta_{\bar{\kappa}}] \\ \left(\frac{E-m}{\pi p}\right)^{1/2}\sin[pr + \nu\ln(2pr) - \tfrac{1}{2}(\bar{l}+1)\pi + \delta_{\bar{\kappa}}]\end{pmatrix}, \tag{42}$$

where the parameter $\nu = \alpha z E/p$, $z$ being the ionic charge.

Substituting the single-electron expression into the multipole transition amplitude we obtain in the

*1. Single-electron approximation:*

$$T^{(\lambda)}_{JM} = \int d^3r\, w^\dagger_i\vec{\alpha}\cdot\vec{a}^{(\lambda)}_{JM}u_i = i\left(\frac{2\pi^2}{Ep}\right)^{1/2}\left(\frac{(2J+1)(J+1)}{J}\right)^{1/2}\frac{\omega^J}{(2J+1)!!}\sum_{\bar{\kappa}m}(\chi^\dagger_\nu\Omega_{\bar{\kappa}\bar{m}}(\hat{p}))(-1)^{\bar{j}-\bar{m}}\begin{pmatrix}\bar{j} & J & j \\ -\bar{m} & M & m\end{pmatrix}i^{1-\bar{l}}e^{i\delta_{\bar{\kappa}}}\langle\bar{a}\|Q^{(\lambda)}_J\|a\rangle. \tag{43}$$

In Eq. (43) the symbol $\langle\bar{a}\|Q^{(\lambda)}_J\|a\rangle$ designates the reduced matrix element of an electric or magnetic multipole operator between an initial state $a = (n\kappa)$ and a final state (energy scale normalized) $\bar{a} = (E,\bar{\kappa})$. This reduced matrix element may be expressed in terms of a radial integral:

$$\langle\bar{a}\|Q^{(\lambda)}_J\|a\rangle = (-1)^{j+1/2}[\bar{j}][j]\begin{pmatrix} j & \bar{j} & J \\ -\tfrac{1}{2} & \tfrac{1}{2} & 0\end{pmatrix} \times\pi(\bar{l},l,J-\lambda+1)R^{(\lambda)}_J(\bar{a},a), \tag{44}$$

where $\pi$ is the parity factor previously defined and where $R^{(\lambda)}_J(\bar{a},a)$ are radial integrals written out in detail below.

We refer to the various excited states with a continuum electron $\bar{a} = (E,\bar{\kappa})$ and with an ion having a single hole $a^{-1} = (n\kappa)^{-1}$ as dissociation channels $(a,\bar{a})$. When we solve the coupled RRPA equations (26) and (27) for a dissociation channel, we normalize so that the outgoing part of the wave $(a\to\bar{a})$ agrees asymptotically with the uncoupled excitation $a\to\bar{a}$ given in Eq. (42). Furthermore, we require that the remaining waves $(b,\bar{b}) \neq (a,\bar{a})$ have *no* outgoing parts, asymptotically. With such a normalization we can use Eq. (43) to describe the many-particle RRPA amplitude as well as the

single-particle amplitude, provided we replace the single-particle reduced matrix element by its many-particle generalization, which is found from Eq. (39) to be:

$$\langle \bar{a} \| Q_J^{(\lambda)} \| a \rangle_{\mathrm{RRPA}} = \sum_{\bar{b}} (\langle \bar{b} + \| Q_J^{(\lambda)} \| b \rangle + \langle \bar{b} - \| Q_J^{(\lambda)} \| b \rangle) . \tag{45}$$

The reduced matrix elements $\langle \bar{b} \pm \| Q_J^{(\lambda)} \| b \rangle$ occurring in the many-particle expression are given in terms of radial integrals $R_J^{(\lambda)}(\bar{b}\pm, b)$ by equations (44). These radial integrals can in turn be expressed as

$$R_J^{(\lambda)}(\bar{b}\pm, b) = \int dr (S_{\bar{b}\pm} X_{bJ}^{(\lambda)} + T_{\bar{b}\pm} Y_{bJ}^{(\lambda)}) , \tag{46}$$

where $S_{\bar{b}\pm}$ and $T_{\bar{b}\pm}$ are the large and small components of the perturbed orbitals $y_{\bar{b}\pm}(r)$ (the positive and negative signs refer to the sign of the frequency $\pm\omega$) given in Eq. (23). The functions $X_{bJ}^{(\lambda)}(r)$ and $Y_{bJ}^{(\lambda)}(r)$ are given by

*2. Magnetic multipole ($\lambda=0$)*

$$\begin{pmatrix} X_{bJ}^{(0)}(r) \\ Y_{bJ}^{(0)}(r) \end{pmatrix} = \frac{(2J+1)!!}{\omega^J} \frac{(\kappa+\bar{\kappa})}{J+1} j_J(\omega r) \begin{pmatrix} F_b \\ G_b \end{pmatrix} . \tag{47}$$

*3. Electric multipoles ($\lambda=1$), Coulomb (velocity) gauge*

$$\begin{pmatrix} X_{bJ}^{(1)}(r) \\ Y_{bJ}^{(1)}(r) \end{pmatrix} = \pm \frac{(2J+1)!!}{\omega^J} \left[ \frac{(\kappa-\bar{\kappa})}{J+1} \left( j_J'(\omega r) + \frac{j_J(\omega r)}{\omega r} \right) \times \begin{pmatrix} F_b \\ G_b \end{pmatrix} + \frac{J j_J(\omega r)}{\omega r} \begin{pmatrix} F_b \\ -G_b \end{pmatrix} \right] . \tag{48a}$$

*4. Electric multipoles ($\lambda=1$), length gauge*

$$\begin{pmatrix} X_{bJ}^{(1)}(r) \\ Y_{bJ}^{(1)}(r) \end{pmatrix} = \frac{(2J+1)!!}{\omega^J} \times \left[ j_J(\omega r) \begin{pmatrix} G_b \\ F_b \end{pmatrix} \pm \frac{(\bar{\kappa}-\kappa)}{J+1} j_{J+1}(\omega r) \begin{pmatrix} F_b \\ G_b \end{pmatrix} \pm j_{J+1}(\omega r) \begin{pmatrix} F_b \\ -G_b \end{pmatrix} \right] . \tag{48b}$$

In Eqs. (47) and (48) the functions $G_b(r)$ and $F_b(r)$ are large and small component radial DF orbitals from Eq. (14). The + and − signs in (47) and (48) refer to the + and − frequency contributions, and the angular quantum numbers $\kappa$ and $\bar{\kappa}$ refer to $b$ and $\bar{b}$, respectively. In the single-channel radial integral of Eq. (44), we use Eqs. (47) and (48) with $S_{\bar{b}+}$ and $T_{\bar{b}+}$ replaced by the single-channel radial functions $S_{\bar{a}}$ and $T_{\bar{a}}$ from Eq. (41).

In the low-frequency limit the reduced matrix elements of the electric dipole operator become:

*5. $J^\pi = 1^-$, length gauge, $\omega \to 0$*

$$\langle \bar{b} \pm \| Q_1^{(1)} \| b \rangle = C_1(b, \bar{b}) \int_0^\infty dr \, (S_{\bar{b}\pm} G_b + T_{\bar{b}\pm} F_b) r , \tag{49a}$$

*6. $J^\pi = 1^-$, Coulomb (velocity) gauge, $\omega \to 0$*

$$\langle \bar{b} \pm \| Q_1^{(1)} \| b \rangle = \pm C_1(b, \bar{b}) \frac{1}{\omega} \int_0^\infty dr \, [(\kappa_b - \bar{\kappa}_b + 1) S_{\bar{b}\pm} F_b + (\kappa_b - \bar{\kappa}_b - 1) T_{\bar{b}\pm} G_b] , \tag{49b}$$

where $C_1(\bar{b}, b)$ is the angular factor defined in Eq. (24a).

### C. Angular distribution and cross section, general case

The differential cross section for photoionization is given in terms of the transition amplitude $T$ of Eq. (11) as[18];

$$\frac{d\sigma}{d\Omega} = \frac{Ep}{2\pi\omega} |T|^2 , \tag{50}$$

where $E$ and $p$ are the photoelectron energy and momentum, and where $\omega$ is the photon energy. Decomposing $T$ into multipole components and averaging over photon polarization one finds

$$\frac{d\sigma}{d\Omega} = \frac{\alpha p E}{2\omega} \sum_{JJ'\lambda\lambda'} [J][J'] i^{J-J'-\lambda+\lambda'} \times [(-1)^{\lambda+\lambda'} T_{J1}^{(\lambda)} T_{J'1}^{(\lambda')*} + T_{J-1}^{(\lambda)} T_{J'-1}^{(\lambda')*}] , \tag{51}$$

where $T_{JM}^{(\lambda)}$ is given in Eq. (43).

If we use the results from Sec. III B to describe the photoionization from a specific subshell $n\kappa$, we find, after summing over spins of the continuum electron and summing over the entire closed subshell $n\kappa$:

$$\frac{d\sigma_{n\kappa}}{d\Omega} = \frac{\alpha\pi}{2\omega} \sum_{L=0}^{\infty} A_L P_L(\cos\theta) , \tag{52}$$

where $\theta$ is the angle between the electron and photon momentum vectors, and where $A_L$ is given by

$$A_L = \sum_{JJ'\lambda\lambda'\bar{\kappa}\bar{\kappa}'} B(J, J', \bar{\kappa}, \bar{\kappa}', L, j) \left( \frac{(J+1)(J'+1)}{JJ'} \right)^{1/2} \frac{\omega^{J+J'}}{(2J-1)!!(2J'-1)!!} \times (i^{J-\lambda-\bar{l}+1} e^{i\delta_{\bar{\kappa}}} \langle \bar{a} \| Q_J^{(\lambda)} \| a \rangle)(i^{J'-\lambda'-\bar{l}'+1} e^{i\delta_{\bar{\kappa}'}} \langle \bar{a}' \| Q_{J'}^{(\lambda')} \| a \rangle)^* , \tag{53}$$

where the coefficient $B$ is

$$B(J,J',\kappa,\kappa',L,j)=(-1)^{j+\bar{j}'-\bar{j}+1/2}[L]^2[\bar{j}][\bar{j}']\begin{pmatrix}\bar{j} & \bar{j}' & L\\ -\frac{1}{2} & \frac{1}{2} & 0\end{pmatrix}\begin{pmatrix}J' & J & L\\ 1 & -1 & 0\end{pmatrix}\begin{Bmatrix}J & J' & L\\ \bar{j}' & \bar{j} & j\end{Bmatrix}\pi(\overline{l\,l}'L)\,. \tag{54}$$

Integrating Eq. (52) over outgoing electron directions we obtain

$$\sigma_{n\kappa}(\omega)=\frac{2\pi^2\alpha}{\omega}A_0=\frac{2\pi^2\alpha}{\omega}\sum_{J\lambda\kappa}\frac{(J+1)}{J(2J+1)}\frac{\omega^{2J}}{[(2J-1)!!]^2}\,|\langle\bar{a}\|Q_J^{(\lambda)}\|a\rangle|^2\,. \tag{55}$$

We have written Eqs. (53) and (55) in terms of the single-electron reduced matrix element; however, as explained in Sec. III B we may replace the single-particle reduced matrix elements by the many-particle expressions (45) to obtain the RRPA results.

### D. Electric dipole transitions: Angular distributions and cross sections

For low photon energies only the electric dipole amplitudes with $J=\lambda=1$ contribute significantly to the cross section. If we restrict our attention to this dipole amplitude we find that only two terms, $A_0$ and $A_2$, are nonvanishing in Eq. (52) so that we may write:

*1. Electric dipole differential cross section*

$$\frac{d\sigma_{n\kappa}}{d\Omega}=\frac{\sigma_{n\kappa}(\omega)}{4\pi}[1-\tfrac{1}{2}\beta_{n\kappa}(\omega)P_2(\cos\theta)]\,, \tag{56}$$

where

$$\sigma_{n\kappa}(\omega)=(2\pi^2\alpha/\omega)A_0 \tag{57a}$$

and

$$\beta_{n\kappa}(\omega)=-2A_2/A_0\,. \tag{57b}$$

Electrons in the subshell $n\kappa$ may be excited to states with $\bar{\kappa}=-\kappa,\kappa\pm1$ by an electric dipole, so we introduce the shorthand notation $D_{j\to\bar{j}}=i^{1-\bar{l}}e^{i\delta_{\bar{\kappa}}}\langle\bar{\kappa}\|Q_1^{(1)}\|\kappa\rangle_{\mathrm{RRPA}}$ for the dipole matrix element to find:

*2. Electric dipole cross section*

$$\sigma_{n\kappa}(\omega)=\frac{4\pi^2\alpha}{3}\,\omega(|D_{j\to j-1}|^2+|D_{j\to j}|^2+|D_{j\to j+1}|^2) \tag{58}$$

and

*3. Electric dipole asymmetry parameter:*

$$\begin{aligned}\beta_{n\kappa}(\omega)=\Big[&\frac{1}{2}\frac{(2j-3)}{2j}|D_{j\to j-1}|^2-\frac{3}{2j}\left(\frac{2j-1}{2(2J+2)}\right)^{1/2}(D_{j\to j-1}D^*_{j\to j}+\text{c.c.})-\frac{(2j-1)(2j+3)}{(2j)(2j+2)}|D_{j\to j}|^2\\&-\frac{3}{2}\left(\frac{(2j-1)(2j+3)}{2j(2j+2)}\right)^{1/2}(D_{j\to j-1}D^*_{j\to j+1}+\text{c.c.})+\frac{1}{2}\frac{(2j+5)}{(2j+2)}|D_{j\to j+1}|^2\\&+\frac{3}{(2j+2)}\left(\frac{2j+3}{2(2j)}\right)^{1/2}(D_{j\to j}D^*_{j\to j+1}+\text{c.c.})\Big](|D_{j\to j-1}|^2+|D_{j\to j}|^2+|D_{j\to j+1}|^2)^{-1}\,.\end{aligned} \tag{59}$$

The term $D_{j\to j-1}$ is absent for $j=\frac{1}{2}$. Expressions similar to Eqs. (58) and (59) for the relativistic dipole cross section and asymmetry parameter were first derived by Walker and Waber,[10] in the context of single-particle potential theory.

## IV. SOLUTION OF THE RRPA EQUATIONS

### A. Single-channel $V^{(N-1)}_{jj}$ approximation

We concentrate on the excited orbitals describing a state $J^\pi$ and take the radial RRPA equations of Eq. (26) or (27) as the point of departure. Let us disregard entirely the negative-frequency orbitals and concentrate on the positive-frequency parts which describe final-state particle-hole interactions. To simplify the positive-frequency equations for a given orbital $y_{\bar{a}}$ we omit all terms on the right-hand side of Eq. (26) or (27) which couple the channel $(a\to\bar{a})$ to other channels. This approximation leads to a single-channel equation for $y_{\bar{a}}$ which is relativistic counterpart of the nonrelativistic $V^{(N-1)}_{LS}$ approximation.[1] We refer to this simplification as the $V^{(N-1)}_{jj}$ approximation to reflect the fact that the particle and hole $(\bar{a},a)$ are coupled in the $j$-$j$ scheme to give a state $J^\pi$.

To describe the resulting equations it is convenient to introduce a potential $V^{(N-1)}$ to describe the motion of the particle $\bar{a}$ in the field of an ion with a hole $a^{-1}$ in one subshell. We have

*1. Electric case: $(a,\bar{a})\to J^\pi$, $\pi=(-1)^J$*

$$\begin{aligned}V^{(N-1)}y_{\bar{a}}&=V^{(N)}y_{\bar{a}}-\sum_l A(a,a,\bar{a},\bar{a},l,J)\frac{e^2}{r}Y_l(a,a,r)y_{\bar{a}}\\&+\frac{C_J^2(a,\bar{a})}{[J]^2}\frac{e^2}{r}Y_J(a,\bar{a},r)\mathfrak{F}_a\,.\end{aligned} \tag{60}$$

*2. Magnetic case: $(a,\bar{a})\to J^{\pi}$, $\pi=(-1)^{J+1}$*

$$V^{(N-1)}y_{\bar{a}} = V^{(N)}y_{\bar{a}} - \sum_l A(-a,-a,\bar{a},\bar{a},l,J)\frac{e^2}{r}Y_l(a,a,r)y_{\bar{a}}\,. \tag{61}$$

These potentials are obtained from the radial RRPA Eqs. (26) and (27) by omitting those terms which couple the channel $(a,\bar{a})$ to other channels. The potential $V^{(N)}$ is the $N$-electron DF potential of Eq. (15). We decompose $V^{(N-1)}$, into a contribution from the subshell $a$ which has the hole, $V_a^{(N-1)}$, and contributions from the remaining filled shells, $V_b$, $b\neq a$. The contributions from shells $b\neq a$ are precisely those given in Eq. (15), while $V_a^{(N-1)}$ is modified according to Eq. (60). For an electric dipole perturbed state we have

*3. Dipole case ($J^{\pi}=1^-$)*

$$V^{(N-1)}y_{\bar{a}} = V_a^{(N-1)}y_{\bar{a}} + \sum_{b\neq a} V_b y_{\bar{a}}\,, \tag{62a}$$

$$V_a^{(N-1)}y_{\bar{a}} = \sum_{l=0,2,4,\ldots} A_l\frac{e^2}{r}Y_l(a,a,r)y_{\bar{a}} + \sum_{l=1,3,5,\ldots} B_l\frac{e^2}{r}Y_l(a,\bar{a},r)\mathfrak{F}_a\,. \tag{62b}$$

The coefficients $A_l$ and $B_l$ are listed in Table I for convenience. It should be noticed that these angular coefficients can be obtained either by simplifying the RRPA equations in a single-channel approximation as we have done above, or directly from a variational calculation in which $(a,\bar{a})$ are coupled to $J^{\pi}$ and the radial functions varied to find an extremum for the energy.

Introducing the radial $V_{jj}^{(N-1)}$ Hamiltonian

$$H_{\bar{a}}^{(N-1)} = \begin{bmatrix} m - \dfrac{Ze^2}{r} + V^{(N-1)} & \dfrac{d}{dr} - \dfrac{\bar{\kappa}_a}{r} \\ -\left(\dfrac{d}{dr} + \dfrac{\bar{\kappa}_a}{r}\right) & -m - \dfrac{Ze^2}{r} + V^{(N-1)} \end{bmatrix}. \tag{63}$$

We may write the $V_{jj}^{(N-1)}$ equations

$$[H_{\bar{a}}^{(N-1)} - (\epsilon_a+\omega)]y_{\bar{a}} - \sum_b \lambda_{\bar{a}b}\delta_{\bar{\kappa}_a\kappa_b}\mathfrak{F}_b = 0\,, \tag{64}$$

where the Lagrange multipliers are introduced to maintain the orthogonality of $y_{\bar{a}}$ to occupied orbitals having the same angular symmetry.

The solutions to Eq. (64) for closed channels $Q$, i.e., channels $(a,\bar{a})$ with $m-\epsilon_a>\omega$, are exponentially damped at large $r$. The solution for open channels $P$, where $m-\epsilon_a<\omega$, on the other hand, are oscillatory at large $r$. The solution $y_{\bar{a}}(r)$, regular at $r=0$, for an open channel has the asymptotic form given in Eq. (42), with energy $E=\epsilon_a+\omega$. The phase shift $\delta_{\bar{\kappa}}$ in Eq. (42) is the sum of a Coulomb part $\sigma_{\bar{\kappa}}$ and a contribution $\delta_{\bar{\kappa}}^0$ due to the short-range parts of $V_{jj}^{(N-1)}$.

Although these solutions to the $V_{jj}^{(N-1)}$ problem do provide a rough approximation to the RRPA equations in which some of the effects of final-state correlations are accounted for, they are not

TABLE I. One-particle, one-hole $V_a^{(N-1)}$ potential of Eq. (62b) is written

$$V_a^{(N-1)}y_{\bar{a}} = \sum_{l=0,2,\ldots} A_l\frac{e^2}{r}Y_l(a,a,r)y_{\bar{a}} + \sum_{l=1,3,5,\ldots} B_l\frac{e^2}{r}Y_l(a,\bar{a},r)\mathfrak{F}_a\,.$$

| $j_a$ | $j_{\bar{a}}$ | $A_0$ | $A_2$ | $A_4$ | $A_6$ | $B_1$ | $B_3$ | $B_5$ | $B_7$ |
|---|---|---|---|---|---|---|---|---|---|
| $\frac{1}{2}$ | $\frac{1}{2}$ | 1 | | | | $-\frac{1}{9}$ | | | |
| $\frac{1}{2}$ | $\frac{3}{2}$ | 1 | | | | $\frac{1}{9}$ | | | |
| $\frac{3}{2}$ | $\frac{1}{2}$ | 3 | | | | $-\frac{2}{9}$ | | | |
| $\frac{3}{2}$ | $\frac{3}{2}$ | 3 | $-\frac{1}{25}$ | | | $\frac{1}{45}$ | $-\frac{9}{35}$ | | |
| $\frac{3}{2}$ | $\frac{5}{2}$ | 3 | $-\frac{4}{25}$ | | | $\frac{2}{5}$ | $-\frac{4}{35}$ | | |
| $\frac{5}{2}$ | $\frac{3}{2}$ | 5 | $-\frac{4}{25}$ | | | $\frac{1}{5}$ | $-\frac{6}{35}$ | | |
| $\frac{5}{2}$ | $\frac{5}{2}$ | 5 | $-\frac{184}{1225}$ | $\frac{2}{147}$ | | $\frac{1}{35}$ | $-\frac{8}{105}$ | $-\frac{50}{231}$ | |
| $\frac{5}{2}$ | $\frac{7}{2}$ | 5 | $-\frac{10}{49}$ | $-\frac{3}{49}$ | | $\frac{5}{7}$ | $-\frac{1}{7}$ | $-\frac{5}{77}$ | |
| $\frac{7}{2}$ | $\frac{5}{2}$ | 7 | $-\frac{10}{49}$ | $-\frac{3}{49}$ | | $\frac{4}{7}$ | $-\frac{4}{21}$ | $-\frac{20}{231}$ | |
| $\frac{7}{2}$ | $\frac{7}{2}$ | 7 | $-\frac{85}{441}$ | $-\frac{23}{539}$ | $\frac{25}{1287}$ | $\frac{5}{189}$ | $-\frac{3}{77}$ | $-\frac{75}{1001}$ | $-\frac{245}{1287}$ |
| $\frac{7}{2}$ | $\frac{9}{2}$ | 7 | $-\frac{2}{9}$ | $-\frac{1}{11}$ | $-\frac{40}{1287}$ | $\frac{28}{27}$ | $-\frac{12}{77}$ | $-\frac{12}{143}$ | $-\frac{56}{1287}$ |

recommended for practical studies. The primary difficulty of the $V_{jj}^{(N-1)}$ approximation is that the continuum electron is actually coupled to the residual ion in an intermediate coupling much closer to $LS$ than to $jj$. The intermediate-coupling $V^{(N-1)}$ scheme, such as that described in Sec. IV B, remedies the problem with final-state coupling; however, since the intermediate-coupling $V^{(N-1)}$ scheme involves several interacting channels, much of the simplicity of Eq. (64) is lost.

In RRPA calculations we do not use the solutions $y_{\bar{a}}$ of the $V_{jj}^{(N-1)}$ equation to calculate amplitudes, but rather as a first approximation to the solution of the coupled RRPA equations. The $V_{jj}^{(N-1)}$ starting solution is iterated numerically to give a desired final RRPA solution in the channel $(a,\bar{a})$.

### B. Multichannel intermediate-coupling $V^{(N-1)}$ approximation and the truncated RRPA

For practical purposes the full set of RRPA equations are not required; it is often sufficient to truncate the RRPA, retaining only a few subshells which interact significantly. For example, in the study of photoionization of 5$s$ electrons in Xe we may consider the excitation of 5$p$, 5$s$, and 4$d$ electrons and ignore the perturbation of the $1s$, $2s$, ..., $4p$ electrons. The resulting system of coupled equations is referred to as the truncated RRPA equations.

At the first stages of a practical solution to the truncated RRPA equations one may neglect the negative-frequency orbitals. This approximation to the RRPA in which only the positive-frequency orbitals are retained is called the Tamm-Dancoff approximation[12]; the same approximation is also referred to simply as the Hartree-Fock approximation in Ref. 1. In the present study we refer to these positive frequency, truncated RRPA equations as the intermediate-coupling Dirac Fock approximation, $V_{IC}^{(N-1)}$, for reasons to be explained below.

The equations for the $V_{IC}^{(N-1)}$ approximation are written

$$[H_{\bar{a}}^{(N-1)} - (\epsilon_a + \omega)]y_{\bar{a}} = R_{\bar{a}} + \sum_b \lambda_{\bar{a}b}\mathfrak{F}_b , \tag{65}$$

where $H_{\bar{a}}^{(N-1)}$ is the $V_{jj}^{(N-1)}$ Hamiltonian of Eq. (63). The coupling term $R_{\bar{a}}$ may be written down from Eq. (26) or (27) by omitting negative-frequency terms:

*1. Electric case: $J^\pi$, $\pi = (-1)^J$*

$$R_{\bar{a}} = -C_J(a,\bar{a})\sum_{b,\bar{b}}{}' \frac{C_J(b,\bar{b})}{[J]^2}\frac{e^2}{r}Y_J(b,\bar{b},r)\mathfrak{F}_a + \sum_{b,\bar{b},l}{}' A(a,b,\bar{a},\bar{b},l,J)\frac{e^2}{r}Y_l(a,b,r)y_{\bar{b}} . \tag{66}$$

*2. Magnetic case: $J^\pi$, $\pi = (-1)^{J+1}$*

$$R_{\bar{a}} = \sum_{b\bar{b}l}{}' A(-a,-\bar{b},\bar{a},b,l,J)\frac{e^2}{r}Y_l(a,b,r)y_{\bar{b}} . \tag{67}$$

The primes on the sums in Eqs. (66) and (67) indicate that the term $(b,\bar{b}) = (a,\bar{a})$ is to be omitted.

Let us illustrate the relation between the $V_{IC}^{(N-1)}$ approximation and the $V_{jj}^{(N-1)}$ approximation using a simple example. The simplest case that arises in practice is the photoionization of an $ns$ electron in the dipole approximation. The possible excitations are

$$ns \to \epsilon p^* ,$$
$$ns \to \epsilon p ,$$

where $p^*$ and $p$ represent $p_{1/2}$ and $p_{3/2}$ orbitals. From Table I we may write the $V_{ns}^{(N-1)}$ potential as

$$\begin{aligned} V_{ns}^{(N-1)}y_{p^*} &= \frac{e^2}{r}Y_0(ns,ns,r)y_{p^*} - \frac{1}{9}\frac{e^2}{r}Y_1(ns,\epsilon p^*,r)\mathfrak{F}_{ns} , \\ V_{ns}^{(N-1)}y_p &= \frac{e^2}{r}Y_0(ns,ns,r)y_p + \frac{1}{9}\frac{e^2}{r}Y_1(ns,\epsilon p,r)\mathfrak{F}_{ns} . \end{aligned} \tag{68}$$

We may now write out the terms $R_{\bar{a}}$ on the right-hand side of Eqs. (65); restricting to the same two channels we find

$$\begin{aligned} R_{p^*} &= -\frac{\sqrt{8}}{9}\frac{e^2}{r}Y_1(ns,p)\mathfrak{F}_{ns} , \\ R_p &= -\frac{\sqrt{8}}{9}\frac{e^2}{r}Y_1(ns,p^*)\mathfrak{F}_{ns} . \end{aligned} \tag{69}$$

These coupling terms in (69) may be included as part of the $V^{(N-1)}$ potential by modifying the exchange part of the potential to be

$$\begin{aligned} X_{ns}^{(N-1)}y_{p^*} &\to \left(-\frac{1}{9}\frac{e^2}{r}Y_1(ns,p^*,r) + \frac{\sqrt{8}}{9}\frac{e^2}{r}Y_1(ns,p,r)\right)\mathfrak{F}_{ns} , \\ X_{ns}^{(N-1)}y_p &\to \left(\frac{\sqrt{8}}{9}\frac{e^2}{r}Y_1(ns,p^*,r) + \frac{1}{9}\frac{e^2}{r}Y_1(ns,p,r)\right)\mathfrak{F}_{ns} . \end{aligned} \tag{70}$$

The transformation of the $(ns,\epsilon p^*)$ and $(ns,\epsilon p)$ states which leads from $jj$ ($J=1$) coupling to $LS$ ($J=1$) coupling will obviously diagonalize the exchange interaction (70). This transformation is accomplished by the linear relation

$$\begin{aligned} y_{^1P}(r) &= (1/3)^{1/2}y_{p^*}(r) + (2/3)^{1/2}y_p(r) , \\ y_{^3P}(r) &= (2/3)^{1/2}y_{p^*}(r) - (1/3)^{1/2}y_p(r) , \end{aligned} \tag{71}$$

from which one finds

$$X_{ns}^{(N-1)} y_{^1P} = \tfrac{1}{3} Y_1(ns, {}^1P, r)\mathfrak{F}_{ns}\,,$$
$$X_{ns}^{(N-1)} y_{^3P} = -\tfrac{1}{3} Y_1(ns, {}^3P, r)\mathfrak{F}_{ns}\,. \tag{72}$$

We see that the resulting diagonalized exchange interaction has the form of the nonrelativistic $V_{LS}^{(N-1)}$ exchange potential used in Hartree-Fock calculations.[19]

Of course, in the relativistic case the transformation from $jj$ states to $LS$ states only diagonalizes the $V^{(N-1)}$ potential but does not diagonalize the Hamiltonian $H^{(N-1)}$ because of the spin-dependent terms in the remaining parts of $H^{(N-1)}$. The coupled equations (65) will therefore not reduce to $V_{LS}^{(N-1)}$ equations except in situations where spin-orbit effects are absolutely negligible. The resulting $V_{IC}^{(N-1)}$ equations (65) are more realistic than the $V_{jj}^{(N-1)}$ equations of Sec. IV A, since these coupled equations (65) reduce to the proper nonrelativistic limit; furthermore, these equations are more realistic than the $V_{LS}^{(N-1)}$ equations employed nonrelativistically since spin-orbit interactions are properly included.

Equations (65) are therefore seen to be the intermediate coupling $V_{IC}^{(N-1)}$ generalization of the $V_{LS}^{(N-1)}$ equations used nonrelativistically. They are not restricted to coupling electrons of only a single orbital angular momentum but, in fact, couple together all of the channels which are associated with one-particle, one-hole final-state interactions.

In our practical calculations we start with solutions to the $V_{jj}^{(N-1)}$ equations as a lowest approximation and then, as a next step, find solutions to the $V_{IC}^{(N-1)}$ equations, using the scheme outlined in Sec. IV C to determine the resulting photoionization cross section.

The solutions to the $V_{IC}^{(N-1)}$ problem provide an excellent approximation to the positive-frequency truncated RRPA orbitals, and the RRPA orbitals can easily be obtained by iteration starting with the $V_{IC}^{(N-1)}$ solution.

It should be mentioned that the truncated RRPA equations are not independent of gauge, as are the full RRPA equations. Truncated RRPA amplitudes are usually evaluated in both velocity and length gauge. Differences between the velocity and length amplitudes of 5% is typical in truncated RRPA calculations.

### C. *K* matrix and *S* matrix

Let $N_p$ be the number of open channels for a state of given $J^\pi$, i.e., the number of pairs $(a,\bar{a})$ allowed by the angular momentum selection rules having $m - \epsilon_a < \omega$. We construct $N_p$ independent solutions to the RRPA equation (26) or (27). It is convenient to label these solutions with a channel index $i = 1, 2, \ldots, N_p$; in the remainder of this section we use superscripts to represent various channels. Starting with the single-channel approximate $V_{jj}^{(N-1)}$ solution of Sec. IV A we may obtain solutions to the RRPA equations which are regular at the origin, and which have the asymptotic form

$$y_j^{(i)}(r) \underset{r\to\infty}{\longrightarrow} f_j(r)\delta_{ji} + g_j(r)K_{ji}\,,\quad i,j = 1,\ldots,N_p\,, \tag{73}$$

where $f_i(r)$ and $g_i(r)$ are regular and irregular *Coulomb* orbitals, described more fully below. The matrix $K = (K_{ij})$ which we shall show to be symmetric is found once the coupled equations are solved. Relations (73) describe the open-channel orbitals only; the remaining closed-channel orbitals, as well as the negative-frequency orbitals, vanish exponentially at large $r$.

In practical calculations several intermediate steps are required to take the iteration solution based on the $V_{jj}^{(N-1)}$ approximation to the form (73), where the asymptotic behavior is governed by Coulomb orbitals; these steps will be described along with other aspects of the numerical procedure in a companion paper.[20]

The regular Coulomb orbital $f_i(r)$ is a solution to the radial Dirac equation in a pure Coulomb field, $V = -e^2 z/r$, regular at $r = 0$, and normalized in the energy scale; $f_i(r)$ behaves asymptotically as

$$f_i(r) \underset{r\to\infty}{\longrightarrow} \begin{pmatrix} \left(\frac{E+m}{\pi p}\right)^{1/2} \cos\left[pr + \nu\ln(2pr) - (l_i+1)\frac{\pi}{2} + \sigma_i\right] \\ \left(\frac{E-m}{\pi p}\right)^{1/2} \sin\left[pr + \nu\ln(2pr) - (l_i+1)\frac{\pi}{2} + \sigma_i\right] \end{pmatrix}, \tag{74}$$

where $\nu = \alpha z E/p$ with $z$ in the ionic charge, and where $\sigma_i$ is the Coulomb phase shift for the orbital $i$. If we let $f_i(r) = (S_i(r), T_i(r))$ and $g_i(r) = (U_i(r), V_i(r))$ be any two solutions of the radial Dirac equation for a local central potential, then the Wronskian $W(f_i, g_i) = [S_i(r)V_i(r) - T_i(r)U_i(r)]$ is a constant, independent of $r$. Two solutions having a Wronskian different from zero, are said to be *independent* solutions. We may construct a solution $g_i(r)$ to the Coulomb-Dirac equation, independent of $f_i(r)$, to have the asymptotic form

$$g_i(r)\underset{r\to\infty}{\longrightarrow}\begin{bmatrix} -\left(\frac{E+m}{\pi p}\right)^{1/2}\sin\left[pr+\nu\ln(2pr)-(l_i+1)\frac{\pi}{2}+\sigma_i\right] \\ \left(\frac{E-m}{\pi p}\right)^{1/2}\cos\left[pr+\nu\ln(2pr)-(l_i+1)\frac{\pi}{2}+\sigma_i\right]\end{bmatrix}; \quad (75)$$

the Wronskian is found to be

$$W(f_i,g_i)=1/\pi\,. \quad (76)$$

Later we will require outgoing waves $h_i^+(r)$ and incoming waves $h_i^-(r)$ which are defined by

$$h_i^{\pm}=f_i\mp ig_i\,. \quad (77)$$

The eigenvalues and eigenvectors of $K$ are important in our analysis of the final-state interactions. If we write

$$\sum_j K_{ij}U_{j\alpha}=\lambda_\alpha U_{i\alpha}\,, \quad (78)$$

then the matrix of eigenvectors $U=(U_{i\alpha})$ may be considered to be orthogonal and the real eigenvalue $\lambda_\alpha$ may be parametrized in terms of eigenphases $\delta_\alpha$ using

$$\lambda_\alpha=\tan\delta_\alpha\,. \quad (79)$$

The particular linear combinations of solutions (73) given by

$$Z_j^{(\alpha)}(r)=\sum_i y_j^{(i)}(r)U_{i\alpha}\cos\delta_\alpha\,,\quad j,\alpha=1,\ldots,N_p \quad (80)$$

are called eigenchannel solutions. From Eqs. (73) and (80) one obtains the asymptotic behavior of these eigenchannel solutions:

$$Z_j^{(\alpha)}(r)\underset{r\to\infty}{\longrightarrow}[f_j(r)\cos\delta_\alpha+g_j(r)\sin\delta_\alpha]U_{j\alpha}\,. \quad (81)$$

The "incoming-wave" boundary condition, that the physical solution to the RRPA equations has a normalized outgoing wave in one channel, and incoming waves in all other channels is easily satisfied in terms of the eigenchannel solutions (80).

The desired "incoming" wave solutions are given by the combination

$$W_j^{(k)}(r)=\sum_\lambda Z_j^{(\lambda)}(r)e^{-i\delta_\lambda}U_{k\lambda}\,, \quad (82)$$

and we find using Eqs. (77) and (81):

$$W_j^{(k)}(r)\to\tfrac{1}{2}h_j^+(r)\delta_{jk}+\tfrac{1}{2}h_j^-(r)S_{jk}^*\,, \quad (83)$$

where $h_j^+(r)$ are the outgoing and incoming spherical waves introduced in Eq. (77) and where the unitary $S$-matrix $S=(S_{jk})$ is given by

$$S=U\Lambda\tilde{U}\,, \quad (84)$$

with

$$\Lambda=\mathrm{diag}(e^{2i\delta_\alpha})\,. \quad (85)$$

An alternative expression for $S$ in terms of $K$ is

$$S=(1+iK)(1-iK)^{-1}\,. \quad (86)$$

The unitarity of $S$ follows from the symmetry of the matrix $K$ which in turn is a consequence of the conservation of current in the RRPA.

Indeed, if we go back to the basic RRPA equation (6) and construct the transition current vector associated with two solutions $w_{j+}^{(i)}(\vec{r})$ and $w_{j+}^{(k)}(\vec{r})$ having the same energy $\omega^{(i)}=\omega^{(k)}=\omega$:

$$\vec{j}_{j\pm}^{(i)(k)}=w_{j\pm}^{(i)+}(\vec{r})\vec{\alpha}w_{j\pm}^{(k)}(\vec{r})\,, \quad (87)$$

we find from Eq. (6)

$$\sum_{j=1}^{N}\int_S da\,(\vec{j}_{j+}^{(i)(k)}-\vec{j}_{j-}^{(i)(k)})\cdot\hat{n}=0\,, \quad (88)$$

where the integration is over a surface $S$ with normal $\hat{n}$. In Eqs. (87) and (88) the superscripts refer to solutions in different channels $(i)$ and $(k)$, while the subscripts refer to individual electrons as in Eq. (6). The orbitals $w_{j-}$ are exponentially damped for large $r$ so that their contributions can be omitted for a sufficiently large surface $S$. The orbitals $w_{j+}$ corresponding to open channels $P$ are oscillatory, while those corresponding to closed channels $Q$ are damped. Taking $S$ to be a large sphere, we may replace Eq. (88) by

$$\sum_{j\subset P}\int_S da\,\vec{j}_{j+}^{(i)(k)}\cdot\hat{n}=0\,. \quad (89)$$

If we let $S_j^{(i)}(r)$ and $T_j^{(i)}(r)$ be the large and small component radial functions for the orbitals of the channel solutions described in Eq. (73), then we find that the current conservation law (89) reduces to

$$\sum_{j=1}^{N_p}[S_j^{(i)*}(r)T_j^{(k)}(r)-T_j^{(i)*}(r)S_j^{(k)}(r)]=0 \quad (90)$$

after the angular integration has been carried out. The individual terms in the round brackets are just the Wronskians of Coulomb wave functions and therefore constants. Substituting from Eq. (73) and making use of Eqs. (74) and (75), one finds

$$(1/\pi)(K_{ik}-K_{ki})=0\,, \quad (91)$$

which gives the desired symmetry relations.

From the reduced matrix elements calculated using the numerical solutions (73) which for simplicity we designate as $Q_i$ $(Q_i=\langle\bar{a}\|Q_J^{(\lambda)}\|a\rangle)$ we obtain eigenamplitudes

$$Q^{(\alpha)} = \sum_i Q_i U_{i\alpha} \cos\delta_\alpha \,. \tag{92}$$

Finally we obtain our "incoming-wave" amplitudes by combining eigenamplitudes according to Eq. (84):

$$Q_i^{(\mathrm{in})} = \sum_\alpha e^{i\delta_\alpha} U_{i\alpha} Q^{(\alpha)} \,. \tag{93}$$

Using the expression (55) for the cross section, we have

$$\sigma_{n\kappa}(\omega) = \frac{2\pi^2\alpha}{\omega} \sum_{J\lambda} \frac{(J+1)\omega^{2J}}{J(2J+1)[(2J-1)!!]^2} \sum_i |Q_i^{(\mathrm{in})}|^2 , \tag{94}$$

where the final sum is over those channels ($i$) which leave the ion in a state $n\kappa$. If we sum over *all* open channels the cross section takes on a particularly simple form in terms of eigenamplitudes $Q^{(\alpha)}$:

$$\sigma = \sum_{n\kappa} \sigma_{n\kappa}(\omega) = \frac{2\pi^2\alpha}{\omega} \sum_{J\lambda\alpha} \frac{(J+1)\omega^{2J}}{J(2J+1)[(2J-1)!!]^2} |Q^{(\alpha)}|^2 , \tag{95}$$

where the sum is over all eigenamplitudes, $a = 1, 2, \ldots, N_p$.

## V. SUMMARY

We have presented a complete, detailed description of the relativistic random-phase approximation and the application of this theory to the photoionization of atoms. Explicit coupled RRPA radial equations for electric and magnetic multipole transitions are derived and are given in Eqs. (26) and (27); formulas for the photoionization cross sections and angular distributions are presented in Eqs. (55) and (53), respectively. The question of choosing an effective potential for photoelectrons in a relativistic theory and the method of solution of the RRPA equations are explained in Sec. IV.

Results of the applications of this theory to the photoionizations of heliumlike and beryllium like ions,[21] the theoretical asymmetry parameter $\beta$ for the 5$s$ electrons[7(b)] and the branching ratio[6(a)] $4d_{5/2}$:$4d_{3/2}$ of xenon atoms have been reported. In a following paper, the results of RRPA calculations for other rare-gas atoms are presented.

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