Electron correlations and spin-orbit interaction in two-photon ionization of closed-shell atoms: A relativistic time-dependent Dirac-Fock approach

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Electron-correlation and spin-orbit-interaction effects are known to play an important role in the quantitative description of multiphoton ionization of heavy atoms. In this paper an *ab initio* approach to two-photon ionization (2PI) of closed-shell atoms in the framework of the relativistic time-dependent Dirac-Fock theory is proposed. This formulation is known to contain important electron-correlation corrections and includes the spin-orbit interaction by use of relativistic wave functions. Computational results for nonresonant 2PI total cross sections of the rare gases are given. The approach is suitable for calculations of angular distributions, branching ratios, and autoionizing resonances.

I. INTRODUCTION

Multiphoton ionization (MPI) of complex atoms, in particular of the rare gases, has been of continuous theoretical and experimental interest during recent few years.[1-5] Experimental progress is stimulated by the availability of pulsed tunable uv lasers, which allow the investigation of frequency-dependent properties in few-photon ionization of atoms with high ionization potentials. As opposed to atoms with a single valence electron outside a tightly bound core, a theoretical description of MPI of atoms with several valence electrons and closed-shell atoms poses two particular challenges to the theorist: First, electron correlations have to be taken into account in a manner more detailed than a model potential can achieve. Second, for heavy atoms, electrons will have relativistic velocities close to the nucleus. The most important relativistic effect in this context is the spin-orbit interaction, which is responsible for the fine-structure splitting of levels and ionization thresholds (1.3 eV for xenon), as well as an $\mathbf{L}\cdot\mathbf{S}$ dependence of amplitudes. The relativistic Dirac-Fock Hamiltonian describes the spin-orbit interaction as well as the relativistic contraction of inner orbitals correctly and in a natural manner.

Several theoretical papers have recently addressed the first of these two problems.[1-3] Their results confirm the importance of electron correlations expected from an interpretation of pertinent experiments. For the particular case of two-photon ionization (2PI) of rare gases, a general tendency of a suppression of 2PI cross sections, as compared to older results,[4] is found. Since in none of these studies was the spin-orbit interaction included, however, the positions of the resonances do not agree with experimental energy levels for the heavier atoms. The spectroscopic effects of the spin-orbit interaction on MPI have been treated semiempirically in the framework of the multichannel quantum defect theory[6] (MQDT) for multiphoton autoionization of xenon. It should be noted, though, that nonrelativistic wave functions cannot give an accurate description of photoionization processes in atoms, even if the fine-structure splitting of thresholds is included, e.g., by using experimental thresholds. For single-photon ionization of rare-gas atoms, it has been demonstrated that usage of relativistic wave functions (i.e., inclusion of spin-orbit effects in the wave functions) leads to a substantial improvement of single-photon amplitudes, in particular, the branching ratios for ionization into the $P_{3/2}$ versus $P_{1/2}$ channels.[7]

It is the purpose of this paper to formulate and test a theoretical approach to MPI of closed-shell atoms (i.e., the rare gases), which accounts for electron correlations as well as spin-orbit interactions. We have chosen the relativistic time-dependent Dirac-Fock (TDDF) method, which is closely related to the relativistic random-phase approximation (RRPA). The RRPA is known to give accurate matrix elements, autoionization spectra, and reactance matrices for single-photon ionization of heavy rare-gas atoms.[7] The TDDF is a generalization of the RRPA allowing an extension to arbitrary order in the external field. The equations resulting from an order-by-order expansion of the TDDF equations are formally closely related to the approach of inhomogeneous differential equations,[8] which are often called Dalgarno-Lewis equations.

Our paper is organized as follows: in Sec. II the equations of the relativistic TDDF model are derived and linearized. In Sec. III these equations are decomposed in terms of angular momentum eigenstates. The equations are applied to the problem of 2PI of rare-gas atoms in Sec. IV, and results for the simplest case, i.e., 2PI with final-state energies above both fine-structure components of the P threshold, are given. Section V gives a short summary and conclusions.

II. RELATIVISTIC TIME-DEPENDENT DIRAC-FOCK MODEL

Our formal derivation of the TDDF equations is similar to the treatment by Smet, Tillieu, and van Groenendael,[9] with a slightly simplified treatment of the Lagrange multipliers. In Sec. II A the derivation and order-by-order expansion of the TDDF equations is given. The resulting equations are reduced to radial equations by means of angular momentum algebra in Sec. II B.

A. TDDF equations

We start with the time-dependent Schrödinger or Dirac equation (the particular form of the kinetic energy operator and the external perturbation is unimportant in the context of this section) for an N-particle wave function $\Psi(t)$ (we omit the spatial and spin coordinates for brevity)

$$\left[-i\frac{\partial}{\partial t}+H_0+\mathcal{V}(t)\right]\Psi(t)=0 , \tag{2.1}$$

which is to be solved approximately in a model space subject to the normalization constraint

$$\langle\Psi(t)|\Psi(t)\rangle=1 . \tag{2.2}$$

Here, H_0 is the Hamiltonian of the unperturbed atom

$$H_0=\sum_{i=1}^{N}\left[t_0(i)-\frac{Z}{r_i}\right]+\sum_{\substack{i,j\\ i<j}}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} , \tag{2.3}$$

where the term in large parentheses is the single-particle Hamiltonian $h_0(i)$, consisting of the kinetic energy operator $t_0(i)$ of the electron with the spatial and spin coordinates $x_i=(\mathbf{r}_i,m_{s_i})$, $r_i=|\mathbf{r}_i|$, and the potential energy Z/r_i of the electron in the field of the nucleus with the nuclear charge Z. The external perturbation $\mathcal{V}(t)$ is a single-body operator

$$\mathcal{V}(t)=\sum_{i=1}^{N}V(\mathbf{r}_i,t) . \tag{2.4}$$

The TDDF model space is defined by restricting $\Psi(t)$ to those time-dependent wave functions which can be represented by a single Slater determinant of time-dependent single-particle wave functions (orbitals) $u_a(x,t)$

$$\Psi(t)\equiv(N!)^{-1/2}\sum_{p\in\mathrm{perm}(N)}\left[\mathrm{sgn}(p)\prod_i u_{a_i}(x_{p(i)},t)\right] . \tag{2.5}$$

Here, $u_{a_1},\ldots,u_{a_N}$ are a family of N time-dependent orbitals identified by labels $a_1,\ldots,a_N$. In the following, we will often omit the argument x in writing the orbitals u_a for brevity. The summation $p\in\mathrm{perm}(N)$ extends over all permutations of the set $\{1,\ldots,N\}$. Note that the expectation value of a single-body operator $\mathcal{O}=\sum_i o(x_i)$, such as the charge or current density, is the sum of the single-body expectation values

$$\langle\psi(t)|\mathcal{O}|\psi(t)\rangle=\sum_a\langle u_a(t)|o|u_a(t)\rangle .$$

We make use of this property in later sections. A sufficient condition for satisfying the normalization (2.2) is that

$$\langle u_a(t)|u_b(t)\rangle=\delta_{ab} . \tag{2.6}$$

Note that all sets of orbitals that define the same many-body wave function [Eq. (2.5)] are related to each other by similarity transforms. Therefore condition (2.6) does not impose any additional restrictions upon the model space.

The time-dependent Hartree-Fock procedure, requiring that the functional

$$I(t)=\left\langle\Psi(t)\left|-i\frac{\partial}{\partial t}+H_0+\mathcal{V}(t)\right|\Psi(t)\right\rangle$$

be stationary under infinitesimal variations of the orbitals $u_a(t)\rightarrow u_a(t)+\delta u_a(t)$, is now carried through in a manner fully analogous to the time-independent procedure and yields the time-dependent Hartree-Fock equation

$$\left[-i\frac{\partial}{\partial t}+h_0+W[u_b(t),u_b(t)]+V(t)\right]u_a(t)=\sum_b\lambda_{ab}(t)u_b(t) . \tag{2.7}$$

The Lagrange multipliers $\lambda_{ab}(t)$ maintain the orthogonality condition of the orbitals (2.6) in the unrestricted variation that corresponds to solving a differential equation. As an abbreviation for the various Hartree-Fock-type potential terms in the subsequent sections, we introduce a generalized Hartree-screening function defined as follows: if x_b and y_b are some arbitrary sets of orbitals, the index b ranging from a_1 to a_N, and z is an arbitrary orbital, the functional $W[\ ,\ ]$ is defined by

$$(W[x_b,y_b]z)(\mathbf{r})\equiv\sum_b\int d\mathbf{r}'\left[x_b^\dagger(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}y_b(\mathbf{r}')z(\mathbf{r})-x_b^\dagger(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}z(\mathbf{r}')y_b(\mathbf{r})\right] . \tag{2.8}$$

For the following argument, we restrict our attention to the relativistic Dirac equation.[10] We are going to show that the TDDF equation has the same behavior under gauge transformations of an externally applied electromagnetic field as the equation for a single electron moving in a local electrostatic potential $V_0(\mathbf{r})$

$$i\hbar\frac{\partial u}{\partial t}=[c\boldsymbol{\alpha}\cdot(\mathbf{p}-e\,\mathbf{A})+\beta mc^2+e\varphi+V_0]u \tag{2.9}$$

(in rational units, $\boldsymbol{\alpha},\beta$ are the Dirac-Pauli spin matrices),

which is form invariant under a transformation of the four-component spinor $u(\mathbf{r},t)$ and the external potentials $\mathbf{A}(\mathbf{r},t)$ and $\varphi(\mathbf{r},t)$, using a gauge function $\chi(\mathbf{r},t)$

$$\tilde{\mathbf{A}}=\mathbf{A}+\nabla\chi, \quad \tilde{\varphi}=\varphi+\partial\chi/\partial t \ , \tag{2.10}$$

$$\tilde{u}=e^{ie\chi}u \ . \tag{2.11}$$

Equation (2.7) is a generalization of Eq. (2.9): V_0 is replaced by $W[u_b(t),u_b(t)]$, and $V(t)=-e\boldsymbol{\alpha}\cdot\mathbf{A}+e\varphi$. The transformation of the external potentials in the TDDF equation is defined by Eq. (2.10), and the orbitals are transformed according to Eq. (2.11); this means, for all orbitals a, $\tilde{u}_a(\mathbf{r},t)=e^{ie\chi(\mathbf{r},t)}u_a(\mathbf{r},t)$. Since the phase factor $e^{ie\chi}$ is common to all orbitals, it may be factored out in front of the Hartree-Fock potential

$$W[e^{ie\chi}u_b,e^{ie\chi}u_b]e^{ie\chi}u_a=e^{ie\chi}W[u_b,u_b]u_a \ . \tag{2.12}$$

This renders the gauge discussion of the TDDF equation (2.7) identical to that of the single-particle Dirac equation (2.9), and it can easily be shown that Eqs. (2.10) and (2.12) constitute a symmetry transform of the TDDF equation (2.7). The observables of the TDDF, namely, the electronic current and charge densities

$$\rho(\mathbf{r},t)=\sum_a eu_a^\dagger(\mathbf{r},t)u_a(\mathbf{r},t) \tag{2.13a}$$

and

$$\mathbf{j}(\mathbf{r},t)=\sum_a ecu_a^\dagger(\mathbf{r},t)\boldsymbol{\alpha}u_a(\mathbf{r},t) \tag{2.13b}$$

are evidently invariant under these transformations. Since the identity of two power-series expansions in an independent variable x (in our case the field amplitude E_0) implies the equality of all coefficients of x, we can conclude that this gauge invariance will also hold true *order by order* in the perturbational expansion of the TDDF equation, which is presented in Sec. II B.

For multiphoton ionization with visible and near-visible uv light, the wavelength of the external radiation field is much larger than the dimensions of the atom, which allows one to describe the interaction of the atom with the radiation field in the dipole approximation. In Coulomb gauge, the potentials for an externally applied field $\mathbf{E}(t)=E_0\hat{\boldsymbol{\epsilon}}e^{\mathbf{k}\cdot\mathbf{r}-\iota\omega t}+\text{c.c.}$ (E_0 is the amplitude, $\hat{\boldsymbol{\epsilon}}$ the polarization unit vector of the field) are $\mathbf{r}$ independent in the dipole approximation

$$\mathbf{A}(\mathbf{r},t)\equiv\mathbf{A}(\mathbf{0},t)=\frac{i}{\omega}E_0\hat{\boldsymbol{\epsilon}}e^{-i\omega t}+\text{c.c.}, \quad \varphi(\mathbf{r},t)=0 \ , \tag{2.14}$$

which leads to the *dipole velocity form* of the interaction operator $V(t)=-e\,\mathbf{A}\cdot\boldsymbol{\alpha}+e\varphi$. A transformation of these potentials with the gauge function $\chi(\mathbf{r},t)=-(i/\omega)E_0\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}e^{-i\omega t}+\text{c.c.}$ cancels the vector part of the external potential and yields

$$\mathbf{A}(\mathbf{r},t)=0, \quad \varphi(\mathbf{r},t)=-E_0\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}e^{-i\omega t}+\text{c.c.} \ , \tag{2.15}$$

which is the *dipole length form* of $V(t)$.

B. Perturbative and harmonic expansion of the TDDF equations

We assume a perturbing external potential purely harmonic in time

$$V(t)=V^+e^{-\iota\omega t}+V^-e^{+i\omega t} \ . \tag{2.16}$$

The time-independent operators $V^\pm$ satisfy $V^-=(V^+)^\dagger$ to ensure Hermiticity of $V(t)$. Consistent with the harmonic perturbation we expand $u_a(t)$ in powers of $e^{-i\omega t}$ and orders of perturbation theory in $V^\pm$

$$u_a(x,t)=e^{-\iota\epsilon_a t}\sum_{k=0}^{\infty}\sum_{f=-k}^{k}u_a^{(k)f}(x)e^{-if\omega t} \ , \tag{2.17}$$

where k indicates the order of perturbation theory in the external perturbation $V(t)$, and f denotes the harmonic components of the perturbed wave function $u_a(t)$. The meaning of ϵ_a, which is an arbitrary parameter here, will be clarified in the discussion of the zeroth-order equation. We call the time-independent orbitals $u_a^{(k)f}(x)$ the "kth-order, f-frequency" components of $u_a(x,t)$. Likewise, we expand the Lagrange multipliers

$$\lambda_{ab}(t)=e^{-\iota\epsilon_a t}\sum_{k,f}\lambda_{ab}^{(k)f}e^{-if\omega t} \ . \tag{2.18}$$

We insert the wave functions and lagrange multipliers Eqs. (2.17) and (2.18) into Eq. (2.7), and separate terms of identical order in $V^\pm$ that have identical time dependence. The resulting equations define a recurrence in k and f, starting at $k=0$ and $f=0$. After inserting, it is seen that the pure harmonicity of the perturbation Eq. (2.16) limits the expansion (2.17) to terms for which $k+f$ is even. All other components are decoupled and thus zero. For convenience, we use the following abbreviations:

$$\begin{aligned} &u_a\equiv u_a^{(0)0}, \quad v_a^\pm\equiv u_a^{(1)\pm1} \ , \\ &w_a^0\equiv u_a^{(2)0}, \quad w_a^\pm\equiv u_a^{(2)\pm2} \ . \end{aligned} \tag{2.19}$$

The $k=0$, $f=0$ term of the expansion yields

$$(h_0-\epsilon_a+W[u_b,u_b])u_a=\sum_b\lambda_{ab}^{(0)0}u_b \ , \tag{2.20}$$

the well-known single-configuration Dirac-Hartree-Fock equation for an unperturbed atom, where u_a are the usual time-independent Dirac-Hartree-Fock orbitals. The parameters ϵ_a obtain their usual meaning of eigenenergies for the orbitals u_a if we require that the diagonal Lagrange multipliers $\lambda_{aa}^{(0)0}$ be zero. Equation (2.20) is to be solved subject to the normalization constraint

$$\langle u_a|u_b\rangle=\delta_{ab} \ , \tag{2.21}$$

which is obtained from the $k=0$, $f=0$ term of Eq. (2.6) after insertion of the expansion Eq. (2.17).

Proceeding to the first order, we obtain the equation

$$\{h_0-(\epsilon_a\pm\omega)+W[u_b,u_b]\}v_a^{\pm}+(W[v_b^{\mp},u_b]+W[u_b,v_b^{\pm}])u_a + V^{\pm}u_a=\sum_b(\lambda_{ab}^{(1)\pm 1}u_b+\lambda_{ab}^{(0)0}v_b^{\pm}) , \tag{2.22}$$

subject to the normalization constraint

$$\langle v_a^{\mp}|u_b\rangle+\langle u_a|v_b^{\pm}\rangle=0 . \tag{2.23a}$$

This normalization condition does not define the solution to Eq. (2.22) uniquely. If we replace $v_a^{\pm}$ by $v_a^{\pm}+\sum_b \alpha_{ab}^{\pm}u_b$, where $\alpha_{ab}^{\pm}+\alpha_{ba}^{\mp *}=0$, the new functions are again solutions of Eq. (2.22), with $\lambda_{ab}^{(1)\pm 1}$ replaced by $\lambda_{ab}^{(1)\pm 1}+[\epsilon_b-(\epsilon_a\pm\omega)]\alpha_{ab}^{\pm}$. A convenient choice of a particular realization of Eq. (2.23a) is the requirement that the perturbed orbitals $v_a^{\pm}$ be orthogonal to all initial-state orbitals

$$\langle u_a|v_b^{\pm}\rangle=0 . \tag{2.23b}$$

This choice has the practical benefit that in a numerical procedure to solve Eq. (2.22) the solutions are guaranteed not to be dominated by arbitrarily growing components proportional to occupied orbitals, which could otherwise lead to a loss of numerical significance. Equation (2.22), solved with the orthogonality condition (2.23b), is structurally *identical* to the equation discussed in Ref. 11, so all the analysis and discussions of that paper also apply here. In a recently published review on RRPA the question of the inclusion of solutions with negative Dirac energy (positron solutions) into the expansion of RRPA states in terms of Dirac-Fock eigenfunctions is discussed.[12]

We call Equation (2.22) the *inhomogeneous RRPA equation.* This is an inhomogeneous equation which is linear in a solution vector whose components are composed of (v_a^{+},v_a^{-*}). The equations are driven by the inhomogeneity $V^{\pm}u_a$. The Lagrange multipliers $\lambda_{ab}^{(1)\pm 1}$ project out components parallel to initial-state orbitals from the solution.

To discuss the properties of the solutions of Eq. (2.22), it is useful to compare the inhomogeneous RRPA equation to the homogeneous RRPA equation, i.e., with $V^{\pm}$ set identical to zero. We refer to the homogeneous equation corresponding to (2.22) as $(2.22)_{\rm hom}$ in the following, and denote its solutions by the symbol $y_a^{\pm}$. It will be seen that the homogeneous equation also plays an important role in the numerical determination of multiphoton ionization amplitudes with final states in the continuum, which can be obtained as scalar products of the solution of the homogeneous equation with the respective driving term [in Eqs. (2.22) and (2.24)], i.e., $V^{\pm}u_a$ for single-photon ionization.

In the summation over the orbitals b in Eq. $(2.22)_{\rm hom}$, in the term for which $b=a$, direct and exchange parts of $W[u_b,u_b]y_a^{\pm}$ and $W[u_b,y_b^{\pm}]u_a$ cancel mutually. Therefore the effective potential in Eq. $(2.22)_{\rm hom}$ is a $V(N-1)$ potential converging to $(N-1-Z)/r$. Equation $(2.22)_{\rm hom}$ defines an eigenvalue problem for ω with eigenfrequencies ω_n. The corresponding eigenstates $y_{a,\omega_n}^{\pm}$ correspond to one-particle, one-hole excited or continuum states of the atom. The full wave function of the system is composed of a sum of Slater determinants in which in the ith term the ith orbital in the determinant is $y_{a_i}^{\pm}$ [or $v_{a_i}^{\pm}$ analogously for (2.22)], whereas all other orbitals $j\neq i$ are unperturbed u_{a_j}. Physically, this corresponds to the various dissociation channels of the atom, leaving behind an ionic core with a hole u_{a_i}. The admixtures from various nonequivalent orbitals in these states represent the effects of electron-correlation terms that are included in the RRPA, as compared to purely $((L_cS_c)J_cj)J$ coupled states. Thus the homogeneous equation $(2.22)_{\rm hom}$ yields one or more Rydberg series of eigenstates, each arising from a certain linear combination of core wave functions. Above each threshold $(\epsilon_a+\omega>0)$, we obtain a continuum of states belonging to the corresponding Rydberg series.

The spectrum predicted by RRPA is an approximation of the atomic spectrum. In particular, reactance matrices obtained from RRPA continuum states have their usual meaning and can be used in a multichannel quantum defect theory analysis of resonance series induced by Rydberg states. However, an interpretation of the RRPA eigenstates as approximations to excited-state wave functions of the atom leads to difficulties. It is discussed in Ref. 11 for the example of the first-order RRPA, that in matrix elements $\langle y_{a,\omega_n}^{+}|V^{+}|u_a\rangle+\langle u_a|V^{-}|y_{a,\omega_n}^{-}\rangle$ of an operator $V^{\pm}$ the contributions from the positive-frequency components y_a^{+} to the matrix element can be identified with many-body perturbation theory (MBPT) corrections for excited-state correlations, whereas those from the negative-frequency components y_a^{-} correspond to ground-state correlations. This implies, on the one hand, that RRPA does not neglect correlation corrections for the initial state, as one might conclude upon the first look at Eq. (2.5), which appears like a single configuration. On the other hand, however, RRPA matrix elements of higher order in the external field cannot be identified with terms of MBPT easily. Note, also, that the RRPA does not contain certain higher-order MBPT terms such as double-particle double-hole excitations.

The spectral properties of the homogeneous and inhomogeneous equations are identical: The solution of the inhomogeneous equation has poles at the eigenfrequencies ω_n of the homogeneous equation, since at these frequencies the left-hand side of the equation is singular (definition of an eigenvalue). The wave functions $v_a^{\pm}$ and therefore also the observables $(\rho,\mathbf{j})$ have poles at ω_n.

In Sec. III we expand Eq. (2.22) in terms of angular momentum eigenfunctions, assuming that the initial state is the ground state of a closed-shell atom, and $V(t)$ is an arbitrary multipole operator. Two cases are of particular interest in our context: First, if $V(t)$ is the electric dipole operator, Eq. (2.22) describes one-photon ionization of an atom, which has been investigated in the present formal-

ism for the case of the rare gases in Ref. 13. Second, it will be shown that the inhomogeneity of the second-order equation (2.24) can be split up into terms of well-defined multipolarity. This means that the solution of Eq. (2.24) can be decomposed into terms with well-defined angular momentum, which renders our analysis of 2PI in many respects an extension of the methods used in the context of 1PI.

The equation for the (2)±0 component w_a^0 [Eq. (2.19)], which describes the time-independent second-order response of the atom to the field, is completely decoupled from the equation for $u_a^{(2)\pm 2}=w_a^{\pm}$. Since we are interested in a description of 2PI in only lowest order in the external field in this work, we may ignore w_a^0.

The second order (± 2)-frequency equation is obtained as

$$\{h_0-(\epsilon_a\pm 2\omega)+W[u_b,u_b]\}w_a^{\pm}+(W[w_b^{\mp},u_b]+W[u_b,w_b^{\pm}])u_a$$
$$+(W[v_b^{\mp},u_b]+W[u_b,v_b^{\pm}])v_a^{\pm}+W[v_b^{\mp},v_b^{\pm}]u_a+V^{\pm}v_a^{\pm}=\sum_b(\lambda_{ab}^{(2)\pm 2}u_b+\lambda_{ab}^{(1)\pm 1}v_b^{\pm}+\lambda_{ab}^{(0)0}w_b^{\pm})\ . \quad (2.24)$$

In this equation, the terms in the first line can easily be identified as formally identical with terms in the first line of Eq. (2.22), whereas the inhomogeneity in the second line consists of several components now: the first three terms represent second-order products of the linear response of the atom to the field, whereas the last term $V^{\pm}v_a^{\pm}$ is analogous to the inhomogeneity of Eq. (2.22) if we compare Eq. (2.24) to a second-order "Dalgarno-Lewis" equation.[8] This structure implies that, besides the particular form of the inhomogeneity, most of the analysis, in particular the radial reduction, can be performed in common for the first- and second-order equations (and likewise, higher-order equations).

Equation (2.24) is to be solved subject to the normalization condition

$$\langle w_a^{\mp}|u_b\rangle+\langle v_a^{\mp}|v_b^{\pm}\rangle+\langle u_a|w_b^{\pm}\rangle=0\ . \quad (2.25)$$

The spectroscopy of Eq. (2.24) reflects correctly the intermediate- and final-state resonances. The inhomogeneity of (2.24) has poles at the eigenfrequencies $\omega=\omega_n$ of the homogeneous first-order equation $(2.22)_{\rm hom}$, coinciding with the intermediate-state resonances. The homogeneous equation corresponding to (2.24) (i.e., with $V^{\pm}$ and $v_a^{\pm}$ set identically to zero) is structurally identical to Eq. $(2.22)_{\rm hom}$. Its eigenvalues indicate the positions of final-state resonances.

III. ANGULAR MOMENTUM DECOMPOSITION OF THE TDDF EQUATIONS

The Dirac Hamiltonian h_0 of a particle in a central electrostatic potential $\varphi(r)$ with no external radiation field ($\mathbf{A}=\mathbf{0}$)

$$h_0=c\boldsymbol{\alpha}\cdot\mathbf{p}+\beta mc^2+e\varphi \quad (3.1)$$

commutes with the total angular momentum $\mathbf{J}=\mathbf{L}+\mathbf{S}$ and the parity Π operators. The eigenfunctions of h_0, $\mathbf{J}$ and Π are defined in terms of the two-component spherical spinor

$$\Omega_{\kappa m}(\hat{\mathbf{r}})=\sum_{m_l,m_s}\langle lsm_lm_s|jm\rangle Y_{lm_l}(\hat{\mathbf{r}})\chi_{m_s}\ , \quad (3.2)$$

where κ is the eigenvalue of the operator $K\equiv-(2\mathbf{L}\cdot\mathbf{S}+1)$, which determines angular momentum j and parity π and can assume nonzero positive and negative integer values. The angular momentum quantum numbers j and l are related to κ by

$$\kappa\equiv\begin{cases}-(l+1)=-(j+\frac{1}{2}), & \kappa<0\\ +l=+(j+\frac{1}{2}), & \kappa>0.\end{cases} \quad (3.3)$$

The coefficients $\langle lsm_lm_s|jm\rangle$ in (3.2) are the Clebsch-Gordan coefficients, $Y_{lm}(\hat{\mathbf{r}})$ the spherical harmonics in the Condon-Shortley phase convention, and χ_{m_s}, $m_s=\pm\frac{1}{2}$, is the two-component spinor for a spin-$\frac{1}{2}$ particle. The four-spinor

$$u_{\kappa m}(\mathbf{r})=\frac{1}{r}\begin{bmatrix}ig(r)\Omega_{\kappa m}(\hat{\mathbf{r}})\\ f(r)\Omega_{-\kappa m}(\hat{\mathbf{r}})\end{bmatrix} \quad (3.4)$$

has well-defined parity $\pi=(-1)^l$ and angular momentum j (j and l are always understood as functions of κ). Note that $u_{\kappa m}$ is only in the nonrelativistic limit an eigenfunction of $\mathbf{L}^2$ because it is constructed from two different eigenvalues $l=j\pm\frac{1}{2}$. We insert $u_{\kappa m}$ into the time-independent Dirac equation with a central potential $\varphi(r)$

$$h_0u=\epsilon u\ , \quad (3.5)$$

and obtain the radial Dirac equation

$$(h_0-\epsilon)u_{\kappa m}\equiv\frac{1}{r}\begin{bmatrix}mc^2-\epsilon+e\varphi & \frac{d}{dr}-\frac{\kappa}{r}\\ -\left(\frac{d}{dr}+\frac{\kappa}{r}\right) & -(mc^2+\epsilon-e\varphi)\end{bmatrix}\begin{bmatrix}g(r)\\ f(r)\end{bmatrix}=0\ , \quad (3.6)$$

where the matrix in large parentheses is $h_{0\kappa}$. From Eq. (3.6) can be seen that g and f are real. In the following, we always write radial wave functions as two-component vectors $\binom{g(r)}{f(r)}$. For an electron in the field of an atomic nucleus, φ is the Coulomb potential $V(r)=e\varphi(r)=-\alpha Z/r$, where $\alpha\approx 1/137.036$ is the Sommerfeld fine-structure constant. In the remainder of this work, we use atomic units, where $\hbar=1$, $m_e=1$, $|e|=1$, $a_0=1$, thus $c=1/\alpha$, and shift the energy scale by the electron rest energy $E=\epsilon-m_ec^2$, which leads to the radial Dirac equation in atomic units

$$\begin{bmatrix} -\frac{Z}{r} & \frac{1}{\alpha}\left[\frac{d}{dr}-\frac{\kappa}{r}\right] \\ -\frac{1}{\alpha}\left[\frac{d}{dr}+\frac{\kappa}{r}\right] & -\frac{2}{\alpha^2}-\frac{Z}{r} \end{bmatrix} \begin{bmatrix} g(r) \\ f(r) \end{bmatrix} = E \begin{bmatrix} g(r) \\ f(r) \end{bmatrix} . \tag{3.7}$$

A. Relativistic Coulomb functions

The long-range behavior of the potential for an electron moving in the field of an ionic core is dominated by the Coulomb term $1/r$. Accordingly, the components of the respective wave function, corresponding to the various dissociation channels, will asymptotically converge to solutions of the relativistic Coulomb problem, which has been described in detail in Ref. 13. We adhere to the notation of Ref. 13 for Coulomb functions. The analysis given there can be directly applied to the treatment of the multichannel case (for an introduction, see the review by Seaton[14] for nonrelativistic problems), which has been worked out for RRPA in Ref. 15. We give a short summary in the following.

Any solution to the relativistic Coulomb problem can be expressed as a linear combination of the linearly independent relativistic Coulomb functions $\mathsf{s}_{E\kappa}$ and $\mathsf{c}_{E\kappa}$, defined by their energy, angular momentum, parity, and their behavior at the origin and at infinity, and normalized on the energy scale. Solution $\mathsf{s}_{E\kappa}$ is regular at the origin, $\mathsf{c}_{E\kappa}$ is singular. The continuum solutions depend on the polar angles according to Eq. (3.4), and their radial parts become asymptotically for $r\to\infty$ (in a.u.),

$$\mathsf{s}_{E\kappa} \sim \begin{bmatrix} \left[\frac{E\alpha^2+2}{\pi p}\right]^{1/2} \cos\left[pr+\frac{E\alpha^2+1}{p}\ln 2pr+\delta_\kappa\right] \\ \left[\frac{E\alpha^2}{\pi p}\right]^{1/2} \sin\left[pr+\frac{E\alpha^2+1}{p}\ln 2pr+\delta_\kappa\right] \end{bmatrix} \tag{3.8}$$

and

$$\mathsf{c}_{E\kappa} \sim \begin{bmatrix} -\left[\frac{E\alpha^2+2}{\pi p}\right]^{1/2} \sin\left[pr+\frac{E\alpha^2+1}{p}\ln 2pr+\delta_\kappa\right] \\ \left[\frac{E\alpha^2}{\pi p}\right]^{1/2} \cos\left[pr+\frac{E\alpha^2+1}{p}\ln 2pr+\delta_\kappa\right] \end{bmatrix} , \tag{3.9}$$

where δ_κ is the Coulomb phase defined according to the conventions of Ref. 13 [Eq. (23)]. The detailed behavior of the solutions for $\epsilon<0$ is of no particular relevance for the analysis in this work and can be found in the mentioned paper.

The Wronski determinant of s and c, generally defined by [cf. Eq. (3.4)]

$$W(u_1,u_2)=\det\begin{bmatrix} g_1 & g_2 \\ f_1 & f_2 \end{bmatrix} \tag{3.10}$$

has the constant value

$$W(\mathsf{s},\mathsf{c})=\frac{\alpha}{\pi} , \tag{3.11}$$

independent of the radius r.

B. Angular momentum decomposition of the TDDF equation—outline

We expand the solution functions of Eqs. (2.20), (2.22), and (2.24) into linear combinations of angular momentum eigenfunctions. All factors depending on angular coordinates can be evaluated analytically, and the equations are thus reduced into a system of coupled ordinary integrodifferential equations.

Let us first outline the general procedure for the angular reduction of Eqs. (2.20), (2.22), and (2.24): The first step is to decompose the orbitals into eigenstates of the single-particle angular momentum and parity operators [Eq. (3.4)]. Due to the spherical symmetry of the ground-state Hartree-Fock potential, the unperturbed orbitals u_a have definite angular momentum and can be written as

$$u_a(\mathbf{r})=\frac{1}{r}\begin{bmatrix} ig_a(r)\Omega_{\kappa_a m_a}(\hat{\mathbf{r}}) \\ f_a(r)\Omega_{-\kappa_a m_a}(\hat{\mathbf{r}}) \end{bmatrix} . \tag{3.12}$$

The index $a\equiv(n_a,\kappa_a,m_a)$ uniquely identifies each orbital. The radial functions g_a and f_a depend only on the principal n_a and angular momentum and parity κ_a quantum numbers, but not on the magnetic quantum number m_a. The total angular momentum of the ground state of a closed-shell atom is automatically $J=0$.

The perturbed orbitals x_a (substitute v and w for x) are set up as linear combinations of single-particle wave functions $x^{(J)}_{a\to\bar{a}\pm}$ with definite angular momentum $\bar{a}\equiv(\kappa_{\bar{a}},m_{\bar{a}})$

$$x^{(J)}_{a\to\bar{a}\pm}=\frac{1}{r}\begin{bmatrix} is^{(J)}_{a\to\bar{a}\pm}(r)\Omega_{\kappa_{\bar{a}}m_{\bar{a}}}(\hat{\mathbf{r}}) \\ t^{(J)}_{a\to\bar{a}\pm}(r)\Omega_{-\kappa_{\bar{a}}m_{\bar{a}}}(\hat{\mathbf{r}}) \end{bmatrix} . \tag{3.13}$$

The radial functions s and t have to be determined by solving the resulting radial equations. Each of the $x^{(J)}_{a\to\bar{a}\pm}$, when substituted for u_a into the Slater determinant at the respective location a, gives rise to a one-particle, one-hole product state of a core having angular momentum $J_c=j_a$ and $M_c=-m_a$ and an excited-state orbital with angular momentum $j_{\bar{a}}$ and $m_{\bar{a}}$,

$$x^{(J)}_{a\to\bar{a}\pm}=b^\dagger_{\bar{a}\pm}b_a|g\rangle , \tag{3.14}$$

where $|g\rangle$ is the initial (ground) state and b_a ($b^\dagger_{\bar{a}\pm}$) are the destruction (creation) operators of orbitals a ($\bar{a}\pm$). Consequently, the indices $(n_a,\kappa_a,\kappa_{\bar{a}},J)$ label $((L_cS_c)J_cj)J$ coupled dissociation channels when the product states are coupled to yield states $x^{\pm(J)}_a$ of given total angular momentum J

$$x_a^{\pm(J)}=\sum_{\bar{a},M}(-1)^{j_a+m_{\bar{a}}+J+M}\begin{pmatrix} j_{\bar{a}} & J & j_a \\ -m_{\bar{a}} & -M & m_a \end{pmatrix}$$

$$\times P(J,M)x_{a\to\bar{a}\pm}^{(J)} \ . \tag{3.15}$$

The terms in large parentheses are the Wigner 3-j symbols in the standard phase convention (see, e.g., Ref. 16). The phase factor is arbitrary and has been introduced for notational consistency with earlier work. The term $P(J,M)$ contains the spherical components of the perturbation [see Eq. (3.19)] and coefficients that ensure that the amplitude E_0 of the external field can be factored out from all terms of the equation and thus makes the solutions $x_a^{\pm(J)}$ independent of the strength of the perturbation. For dipole excitation, selection rules restrict J to $J=1$ for the first-order orbitals, and $J=0,2$ for second order. The summation $\bar{a}$ is limited to angular momenta compatible with the triangular $\Delta(j_a,j_{\bar{a}},J)$ and parity $\Pi(l_a,l_{\bar{a}},J)\equiv\frac{1}{2}[1+(-1)^{l_a+l_{\bar{a}}+J}]=1$ selection rules. It follows from the definition of the 3-j symbol that a summation of Slater determinants built up from states $x_a^{\pm(J)}$ over a complete subshell (specified by fixed n_a and κ_a, summing over m_a) has a total angular momentum J. The perturbed orbital $x_a^{\pm}$ is the sum

$$x_a^{\pm}=\sum_J x_a^{\pm(J)} \ . \tag{3.16}$$

The equations governing $x_{a\to\bar{a}\pm}^{\pm(J)}$ will turn out to be decoupled with respect to J.

The orbitals (u_a and $x_a^{\pm}$, where $x_a^{\pm}$ are replaced by $v_a^{\pm}$ or $w_a^{\pm}$ in the following) are inserted into the respective equations. The Coulomb potential is multipole expanded, which yields summations over spherical harmonics and radial Hartree screening functions $\mathcal{R}$ (see the Appendix).

$$\left[h_{0_a}-\epsilon_a+\sum_b[j_b]\mathcal{R}_0[u_b,u_b]\right]u_a-\sum_{b,L}[j_b]\begin{pmatrix} j_a & j_b & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}^2\Pi(l_a,l_b,L)\mathcal{R}_L[u_b,u_a]u_b=\sum_b\lambda_{ab}u_b^0 \ . \tag{3.18}$$

Here $\mathcal{R}_L$, which is defined in Eq. (A2), is the radial part of the 2^L-pole component of the Hartree screening function W of Eq. (2.8), and $[j]\equiv(2j+1)$.

D. The first-order equation

The spherical decomposition of the external interaction defines what has to be substituted for $P(J,M)$. We assume excitation by an electric 2^k-pole potential in length form

$$V^{\pm}(\mathbf{x})=\sum_q V_q^{\pm}C_{k-q}(\hat{\mathbf{r}})\mathcal{L}(r) \ , \tag{3.19}$$

which has to satisfy $V^{\pm}=(-1)^q(V^{\mp})^*$ to ensure Hermiticity. For radiation fields in length approximation, $\mathcal{L}(r)\equiv r^k$, and, in dipole approximation, $V_q^{\pm}=E_0\delta(q,0)$ for linear, $V_q^{\pm}=E_0\delta(q,\pm1)$ for circular polarization, δ being the Kronecker delta and E_0 the amplitude of the external field [Eq. (2.14)]. Although we are exclusively concerned with electric dipole excitation in the remainder of this work, we give the full multipole decomposition of the first-order equation because we want to identify the terms in the first line of the dipole-driven second-order equation (2.24) as monopole and quadrupole terms. Angular decomposition of the driving term

$$V^{\pm}u_a=\sum_q(-1)^qV_q^{\pm}C_{k-q}(\hat{\mathbf{r}})\mathcal{L}(r)u_a(\mathbf{r}) \tag{3.20}$$

yields

$$V^{\pm}u_a=\sum_{\bar{a},q}(-1)^{j_{\bar{a}}-m_{\bar{a}}+q}V_q^{\pm}\begin{pmatrix} j_{\bar{a}} & k & j_a \\ -m_{\bar{a}} & -q & m_a \end{pmatrix}$$

$$\times\langle j_{\bar{a}}\|C_k\|j_a\rangle\mathcal{L}(r)u_{a:\bar{a}}(\mathbf{r}) \tag{3.21}$$

after decomposition. The subscript $a:\bar{a}$ is, for any orbital $u_a\equiv u_{\kappa_a m_a}$ [Eq. (3.4)], defined by

The completeness relation for the spherical spinors

$$\sum_{\kappa,m}\Omega_{\kappa m}(\hat{\mathbf{r}})\int d\mathbf{r}'\frac{1}{r^2}\delta(r-r')\Omega_{\kappa m}^{\dagger}(\hat{\mathbf{r}}')F(\mathbf{r}')=F(\mathbf{r}) \tag{3.17}$$

[where $F(\mathbf{r})$ is an arbitrary two-component spinor] is applied to transform all terms into linear combinations of functions with well-defined angular momentum. The angular matrix elements thus obtained are reduced by the Wigner-Eckart theorem, leading to products of 3-j symbols and reduced matrix elements of spherical harmonics. All summations over doubly occurring magnetic quantum numbers are carried out, and terms

$$\sum_M(-1)^{j_{\bar{a}}-m_{\bar{a}}+J-M}\begin{pmatrix} j_{\bar{a}} & J & j_a \\ -m_{\bar{a}} & -M & m_a \end{pmatrix}P(J,M)$$

are factored out. This factorization is possible because the ground-state Dirac-Fock potential commutes with the total angular momentum operator, and because the perturbed orbitals have been constructed in a way that their angular symmetry imitates that of the inhomogeneity. Finally, terms with identical dependencies on the remaining magnetic quantum numbers m_a, $m_{\bar{a}}$, and $P(J,M)$, and on the angular coordinate $\hat{\mathbf{r}}$ are identified and separated. The resulting equations, which are the desired result, are independent of all magnetic quantum numbers, $\hat{\mathbf{r}}$, and $P(J,M)$, and are decoupled in J.

C. The zeroth-order equation

Let us now carry out the program outlined above, starting with the zeroth-order equation. We postulate that the orbitals u_a be of the form of Eq. (3.12), insert into Eq. (2.20) and follow the reduction steps to obtain the radial Dirac-Fock equation for the unperturbed ground-state orbitals

$$u_{a:\bar{a}}(\mathbf{r})=\frac{1}{r}\begin{bmatrix} ig_a(r)\Omega_{\kappa_{\bar{a}}m_{\bar{a}}}(\hat{\mathbf{r}}) \\ f_a(r)\Omega_{-\kappa_{\bar{a}}m_{\bar{a}}}(\hat{\mathbf{r}}) \end{bmatrix} . \tag{3.22}$$

For consistency in the dependence of all terms of the first-order equation on $\hat{\mathbf{r}}$, q, m_a, and $m_{\bar{a}}$, we define

$$P(J,M)=V_q^{\pm}\delta(k,J)\delta(q,M) , \tag{3.23}$$

and obtain

$$v_a^{\pm}\equiv\sum_{\bar{a},q}(-1)^{j_a+m_{\bar{a}}+k+q}V_q^{\pm}\begin{pmatrix} j_{\bar{a}} & k & j_a \\ -m_{\bar{a}} & -q & m_a \end{pmatrix}v^{(J)}_{a\to\bar{a}\pm} . \tag{3.24}$$

Insertion into (2.22) yields the radial first order TDDF equation for 2^k-pole excitation

$$\left[h_{0_{\bar{a}}}-(\epsilon_a\pm\omega)+\sum_b[j_b]\mathcal{R}_0[u_b,u_b]\right]v^{(J)}_{a\to\bar{a}\pm}-\sum_{\bar{a},b,L}[j_b]\begin{pmatrix} j_{\bar{a}} & j_b & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}^2\Pi(l_{\bar{a}},l_b,L)\mathcal{R}_L[u_b,v^{(J)}_{a\to\bar{a}\pm}]u_{b:\bar{a}}$$
$$+\sum_{b,\bar{b}}\frac{1}{[J]}\langle a\|C_J\|\bar{a}\rangle\langle b\|C_J\|\bar{b}\rangle(\mathcal{R}_J[u_b,v^{(J)}_{b\to\bar{b}\pm}]+\mathcal{R}_J[v^{(J)}_{b\to\bar{b}\pm},u_b])u_{a\bar{a}}$$
$$-\sum_{b,\bar{b},L}\{A(ab,\bar{a}\bar{b};LJ)\mathcal{R}_L[u_b,u_a]v^{(J)}_{b\to\bar{b}\pm:\bar{a}}+A(a\bar{b},\bar{a}b;LJ)\mathcal{R}_L[v^{(J)}_{b\to\bar{b}\pm},u_a]u_{b:\bar{a}}\}$$
$$+\sum_{\bar{a},q}(-1)^{k+1}\langle j_a\|C_k\|j_{\bar{a}}\rangle\mathcal{L}(r)u_{a:\bar{a}}=\sum_b\lambda^{(1)}_{a\to\bar{a}\pm b}\delta(j_{\bar{a}},j_b)u_{b:\bar{a}} . \tag{3.25}$$

Note that in Eq. (3.25), summation indices $(a,b,\bar{b})$ no longer include magnetic quantum numbers. The coefficients $A(\ )$ are defined in Eq. (A7).

E. The second-order equation

For the second-order equation, we restrict our attention to dipole excitation $k=1$. The external driving term is in this case $V^{\pm}v_a^{\pm}$. By letting

$$P(J,M)=\sum_{q,q'}(-1)^{q+q'}\begin{pmatrix} 1 & J & 1 \\ -q' & M & -q \end{pmatrix}V_{q'}^{\pm}V_q^{\pm} \tag{3.26}$$

we have

$$w_a^{\pm}=\sum_{\bar{a},q,q',J,M}V_{q'}^{\pm}V_q^{\pm}(-1)^{j_a+m_{\bar{a}}+J-M+q+q'}\times\begin{pmatrix} j_{\bar{a}} & J & j_a \\ -m_{\bar{a}} & -M & m_a \end{pmatrix}\times\begin{pmatrix} 1 & J & 1 \\ -q' & M & -q \end{pmatrix}w^{(J)}_{a\to\bar{a}\pm} , \tag{3.27}$$

where the summation over $\bar{a}$ is limited to terms satisfying the parity selection rule $\Pi(a,\bar{a},J)=1$. From the selection rules, the symmetry of $V^{\pm}$, and the angular momentum diagrams it is easily concluded that the summation over J is restricted to $J=0,2$. The decomposition is carried through along the same lines as above. The result is the radial equation for dipole excitation in second-order TDDF, where we indicate first-order channels by $a\to\tilde{a}$, $b\to\tilde{b}$, $b\to\hat{b}$, and second-order channels by $a\to\bar{a}$, $b\to\bar{b}$,

$$\left[h_{0_{\bar{a}}}-(\epsilon_a\pm2\omega)+\sum_b[j_b]\mathcal{R}_0[u_b,u_b]\right]w^{(J)}_{a\to\bar{a}\pm}\sum_{\bar{a},b,L}[j_b]\begin{pmatrix} j_{\bar{a}} & j_b & L \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}^2\Pi(l_{\bar{a}},l_b,L)\mathcal{R}_L[u_b,w^{(J)}_{a\to\bar{a}\pm}]u_{b:\bar{a}}$$
$$+\sum_{b,\bar{b}}\frac{1}{[J]}\langle a\|C_J\|\bar{a}\rangle\langle b\|C_J\|\bar{b}\rangle(\mathcal{R}_J[u_b,w^{(J)}_{b\to\bar{b}\pm}]+\mathcal{R}_J[w^{(J)}_{b\to\bar{b}\mp},u_b])u_{a\bar{a}}$$
$$-\sum_{b,\bar{b},L}\{A(ab,\bar{a}\bar{b};LJ)\mathcal{R}_L[u_b,u_a]w^{(J)}_{b\to\bar{b}\pm:\bar{a}}+A(a\bar{b},\bar{a}b;LJ)\mathcal{R}_L[w^{(J)}_{b\to\bar{b}\pm},u_a]u_{b:\bar{a}}\}$$
$$+\sum_{\bar{a}}(-1)^{j_a-j_{\bar{a}}}[J]\begin{Bmatrix} 1 & J & 1 \\ a & \tilde{a} & \bar{a} \end{Bmatrix}\langle\tilde{a}\|C_1\|\bar{a}\rangle\mathcal{L}(r)v_{a\to\tilde{a}\pm:\bar{a}}$$
$$+\sum_{\tilde{a},\bar{b},\tilde{b}}(-1)^{j_a-j_{\bar{a}}}\frac{[J]}{3}\begin{Bmatrix} 1 & J & 1 \\ a & \tilde{a} & \bar{a} \end{Bmatrix}\langle\tilde{a}\|C_1\|\bar{a}\rangle\langle b\|C_1\|\bar{b}\rangle(\mathcal{R}_1[u_b,v_{b\to\tilde{b}\pm}]+\mathcal{R}_1[v_{b\to\tilde{b}\mp},u_b])v_{a\to\tilde{a}\pm:\bar{a}}$$
$$-\sum_{\tilde{a},\bar{b},\tilde{b},L}(-1)^{j_a-j_{\bar{a}}}[J]\begin{Bmatrix} 1 & J & 1 \\ a & \tilde{a} & \bar{a} \end{Bmatrix}\{(-1)^{j_b-j_{\tilde{b}}}A(\bar{a}\tilde{b},\tilde{a}b;L1)\mathcal{R}_L[u_b,v_{a\to\tilde{a}\pm}]v_{b\to\tilde{b}\pm:\bar{a}}$$
$$+A(\bar{a}b,\tilde{a}\tilde{b};L1)\mathcal{R}_L[v_{b\to\tilde{b}\mp},v_{a\to\tilde{a}\pm}]u_{b:\bar{a}}\}$$

$$+\sum_{b,\bar{b},\hat{b}}(-1)^{j_b-j_{\tilde{b}}}\begin{Bmatrix}1 & J & 1\\ \hat{b} & b & \tilde{b}\end{Bmatrix}\langle\hat{b}\|C_J\|\tilde{b}\rangle\langle a\|C_J\|\bar{a}\rangle\mathcal{R}_J[v_{b\to\hat{b}\mp},v_{b\to\bar{b}\pm}]u_{a:\bar{a}}$$

$$-\sum_{b,\bar{b},\hat{b},L}(-1)^{j_b-j_{\tilde{b}}}\begin{Bmatrix}1 & J & 1\\ \hat{b} & b & \tilde{b}\end{Bmatrix}[J]A(a\hat{b},\bar{a}\tilde{b};LJ)\mathcal{R}_L[v_{b\to\hat{b}\mp},u_a]v_{b\to\bar{b}\pm:\bar{a}}$$

$$=\sum_b\lambda^{(2)(J)}_{a\to\bar{a}\pm b}\delta(j_{\bar{a}},j_b)u_{b:\bar{a}}+\sum_{\bar{a},\bar{b},\tilde{b}}(-1)^{j_a+j_{\bar{a}}}\delta(j_{\bar{a}},j_{\tilde{b}})\delta(j_{\tilde{a}},j_b)\begin{Bmatrix}1 & J & 1\\ a & b & \tilde{a}\end{Bmatrix}\lambda^{(1)}_{a\to\bar{a}\pm:b}v_{b\to\tilde{b}\pm:\bar{a}}\ . \quad (3.28)$$

Comparing this equation with Eq. (3.25), we see that, up to $\omega\to 2\omega$, the homogeneous terms of Eq. (3.28) are identical to those of Eq. (3.25). The orbital labels a, $\bar{a}$, etc. in the 6-j-symbols are shorthand for the respective j quantum numbers j_a, $j_{\bar{a}}$, etc. Note that $P(J,M)$ has been defined in a way that the various J components of the equation are decoupled.

F. The homogeneous RRPA equation: Dissociation channels and reactance matrix

As will be shown in Sec. IV, the TDDF amplitude for 1PI and 2PI are obtained from RRPA scalar products of the solution to the homogeneous RRPA equation with the respective inhomogeneity. The analysis given there expresses the asymptotic behavior of solutions to the homogeneous equation in terms of the reactance matrix.[14]

For a given frequency ω, we call the dissociation channels $a\to\bar{a}+$ originating from orbitals with $\epsilon_a+\omega>0$ *open*. All the other positive-frequency and all negative-frequency $a\to\bar{a}-$ channels are *closed*. The closed-channel wave functions have an asymptotically exponential behavior at large r and have to decay exponentially in order for the total wave function to be normalizable. The open-channel wave functions converge asymptotically to a linear combination of continuum Coulomb functions. If there are I_0 open channels, there are I_0 linearly independent solutions that satisfy the regularity condition at the origin. We introduce the label i as an abbreviation for the channel index $a\to\bar{a}\pm$ (so i numbers the components), write $i\in\mathsf{P}$ for open and $i\in\mathsf{Q}$ for closed channels, and define, assuming that J is fixed, the asymptotic behavior of the jth linearly independent solution to the homogeneous equation $y_i^{(j)}\equiv y_{a\to\bar{a}\pm}^{(J)(j)}$ as

$$y_i^{(j)}\xrightarrow[r\to\infty]{}\begin{cases}\mathsf{s}_i\delta_{ij}+\mathsf{c}_iR_{ij} & (i\in\mathsf{P})\\ 0 & (i\in\mathsf{Q}),\end{cases} \quad (3.29)$$

where s_i and c_i are the Coulomb functions with energy and angular momentum identical to those of channel i, and $\underline{R}$ is the reactance matrix.

We show in Sec. IV how the amplitudes of solutions to the inhomogeneous equation can be obtained starting from a complete set of solutions to the homogeneous equations at one given frequency, satisfying the asymptotic condition Eq. (3.29), and the respective inhomogeneity.

IV. TWO-PHOTON IONIZATION OF RARE GASES

In typical multiphoton ionization experiments, observables such as the total current, angular and energy distributions, and spin polarization of photoelectrons are measured. For the physical interpretation of the TDDF equations we adopt the picture of Sommerfeld,[17] where for harmonic perturbations photoionization cross sections and angular distributions are related to the photoelectron current density.

The following derivation is broken up into two parts: first we derive the total and differential multiphoton ionization cross sections assuming that the solutions Eqs. (3.24) and (3.27) to the inhomogeneous equations (3.25) and (3.28) satisfy outgoing partial wave boundary conditions in each open channel. The result is that the cross section and angular distribution coefficients can be expressed as quadratic functions of the asymptotic amplitudes of the outgoing partial waves in each channel. Then we show that, to obtain these amplitudes, it is not necessary to solve Eqs. (2.22),(2.24), and (3.25),(3.28) explicitly under outgoing partial wave boundary conditions. Instead, these amplitudes can be expressed in terms of scalar products of the solutions to the homogeneous equation with the inhomogeneity.

A. Photoelectron current and differential cross section

The total photoelectron current $J_{\rm tot}$ is obtained by integrating the radial component of the current density $\mathbf{j}\cdot\hat{\mathbf{r}}$ over a sphere with large radius r. In the regime of lowest order of perturbation theory in the external field, the total current is proportional to the Nth power of the photon flux density $F=I/\hbar\omega$ in N-photon processes. This allows to define an intensity-independent generalized cross section for N-photon ionization

$$J_{\rm tot}\equiv\lim_{r\to\infty}r^2\int\mathbf{j}\cdot\hat{\mathbf{r}}\,d\hat{\mathbf{r}}=F^N\sigma^{(N)}\ . \quad (4.1)$$

The photon flux F is related to the amplitude of the radiation field E_0 and thus to the perturbation $V(\mathbf{x},t)$ in dipole approximation by

$$F=\frac{1}{2\pi\alpha}\frac{1}{\omega}E_0^2 \quad (4.2)$$

and

$$V(\mathbf{x},t)=E_0\hat{\boldsymbol{\epsilon}}\cdot\mathbf{D}e^{-i\omega t}+\text{c.c.}\ , \quad (4.3)$$

where $\hat{\boldsymbol{\varepsilon}}$ is the polarization unit vector of the radiation field

$$\mathbf{E}(t)=E_0\hat{\boldsymbol{\varepsilon}}e^{-i\omega t}+\text{c.c.}\ , \tag{4.4}$$

and $\mathbf{D}=\sum_i \mathbf{r}_i$ is the dipole operator in length form. The amplitude of the perturbation is $V^{\pm}=E_0\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}$ and therefore $|V_q^{\pm}|=E_0$.

Angular distributions can be represented by the coefficients of expansions of the polar angle dependence of the current in terms of spherical harmonics $C_{KQ}(\hat{\mathbf{r}})$.

$$\frac{d\sigma}{d\omega}\propto\lim_{r\to\infty} r^2\mathbf{j}\cdot\hat{\mathbf{r}}\equiv\sum_{K,Q}\gamma_{KQ}(\mathbf{j})C_{KQ}(\hat{\mathbf{r}})\ , \tag{4.5}$$

$$\gamma_{KQ}(\mathbf{j})=\frac{2K+1}{4\pi}\lim_{r\to\infty} r^2\int d\hat{\mathbf{r}}\,C^*_{KQ}(\hat{\mathbf{r}})\mathbf{j}\cdot\hat{\mathbf{r}}\ . \tag{4.6}$$

Since the contributions to the photoelectron current density $\mathbf{j}(\mathbf{r},t)$ (which is a one-body operator) arising from different orbitals add up incoherently, we need to consider only the contribution $\mathbf{j}_{\hat{a}}$ from one given completely occupied subshell $\hat{a}\equiv(n_a,\kappa_a)$ in the following.

Inserting TDDF orbitals for the wave functions, this partial current is

$$\mathbf{j}_{\hat{a}}(\mathbf{r})=\frac{1}{\alpha}\sum_{m_a}(u_a^{\dagger}\boldsymbol{\alpha}u_a)(\mathbf{r})\ . \tag{4.7}$$

For large r, only open channels contribute to $\mathbf{j}_{\hat{a}}$. Using the notation of Sec. III, Eqs. (3.13) and (3.15), to unify the treatment of 1PI and 2PI as long as possible, we obtain

$$\begin{aligned}\gamma_{KQ}(\hat{a})&=\lim_{r\to\infty}\frac{2K+1}{4\pi\alpha}r^2\sum_{m_a}\int d\hat{\mathbf{r}}[u_a^{\dagger}\boldsymbol{\alpha}\cdot\hat{\mathbf{r}}C^*_{KQ}(\hat{\mathbf{r}})u_a](\mathbf{r})\\&=\lim_{r\to\infty}\frac{2K+1}{4\pi\alpha}r^2\sum_{m_a}\int d\hat{\mathbf{r}}[x_a^{+\dagger}\boldsymbol{\alpha}\cdot\hat{\mathbf{r}}C^*_{KQ}(\hat{\mathbf{r}})x_a^{+}](\mathbf{r})\\&=\lim_{r\to\infty}\frac{2K+1}{4\pi\alpha}\sum_{m_a,\bar{a},\bar{a}',Q,Q',J,J',M,M'}(-1)^{j_{\bar{a}}-j_{\bar{a}'}}\\&\quad\times\begin{pmatrix}j_{\bar{a}'}&J'&j_a\\-m_{\bar{a}'}&-M'&m_a\end{pmatrix}\begin{pmatrix}j_{\bar{a}}&J&j_a\\-m_{\bar{a}}&-M&m_a\end{pmatrix}\\&\quad\times P(J',M')^*P(J,M)\left\{r^2\int d^2\hat{\mathbf{r}}[x^{(J')\dagger}_{a\to\bar{a}'+}\boldsymbol{\alpha}\cdot\hat{\mathbf{r}}C^*_{KQ}(\hat{\mathbf{r}})x^{(J)}_{a\to\bar{a}+}](\mathbf{r})\right\}\ .\end{aligned} \tag{4.8}$$

The term in large curly braces, I, is written out in terms of upper and lower components [Eq. (3.13)] and the identity $\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\Omega_{\kappa m}(\hat{\mathbf{r}})=-\Omega_{-\kappa m}(\hat{\mathbf{r}})$ is used to transform I into a radial expression and an angular integral which is reduced by the Wigner-Eckart theorem. We obtain

$$\begin{aligned}I=i&\left[s^{(J')}_{a\to\bar{a}'+}t^{(J)}_{a\to\bar{a}+}-t^{(J')}_{a\to\bar{a}'+}s^{(J)}_{a\to\bar{a}+}\right](-1)^{j_{\bar{a}'}-m_{\bar{a}'}+Q}\\&\times\begin{pmatrix}j_{\bar{a}'}&K&j_{\bar{a}}\\-m_{\bar{a}'}&-Q&m_{\bar{a}}\end{pmatrix}\langle\bar{a}'\|C_K\|\bar{a}\rangle\ .\end{aligned} \tag{4.9}$$

The reduced matrix element is between functions $\bar{a}'$ and $\bar{a}$ that arise from the same initial states and therefore have the same parity, which implies that $K\in 2\mathbb{N}$, as we expect for symmetry reasons. We recognize in Eq. (4.9) that the term in large parentheses is the relativistic Wronski determinant $W(x^{(J')*}_{a\to\bar{a}'+},x^{(J)}_{a\to\bar{a}+})$ as defined in Eq. (3.10).

Given that the initial condition is a bound state, the perturbed orbitals must satisfy outgoing spherical wave boundary conditions. For large r, the potential becomes Coulombic, and the driving terms vanish, thus $x^{(J)}_{a\to\bar{a}+}$ converges to a linear combination of Coulomb functions

$$x^{(J)}_{a\to\bar{a}+}\xrightarrow[r\to\infty]{}A^{(J)}_{a\to\bar{a}+}(\mathsf{c}_{a\to\bar{a}+}+i\mathsf{s}_{a\to\bar{a}+})\ , \tag{4.10}$$

with — as yet undetermined — complex amplitudes $A^{(J)}_{a\to\bar{a}+}$. Since $W(\mathsf{s},\mathsf{c})=(\alpha/\pi)$ [Eq. (3.11)], we obtain the final result for the radial term

$$W(x^{(J')*}_{a\to\bar{a}'+},x^{(J)}_{a\to\bar{a}+})\xrightarrow[r\to\infty]{}A^{(J')*}_{a\to\bar{a}'+}A^{(J)}_{a\to\bar{a}+}\frac{2\alpha}{i\pi}\times e^{i(\delta_{a\to\bar{a}+}-\delta_{a\to\bar{a}+'})}\ , \tag{4.11}$$

where $\delta_{a\to\bar{a}+}$ is the Coulomb phase of $\mathsf{c}_{a\to\bar{a}+}$ and $\mathsf{s}_{a\to\bar{a}+}$, as it occurs in Eqs. (3.8) and (3.9). The phase factor arises from taking the Wronski determinant of Coulomb functions of the same energy, but different angular momentum.

Now we sum over all doubly occurring magnetic quantum numbers and obtain, after factoring out a 6-j symbol, that

$$\begin{aligned}\gamma_{KQ}(\hat{a})=\frac{2k+1}{2\pi^2}\sum_{J,J',M,M',\bar{a},\bar{a}'}&(-1)^{j_a+j_{\bar{a}}+M'}\begin{Bmatrix}K&J'&J\\a&\bar{a}&\bar{a}'\end{Bmatrix}\langle\bar{a}'\|C_K\|\bar{a}\rangle\begin{pmatrix}J&K&J'\\M&Q&-M'\end{pmatrix}P(J',M')^*\\&\times P(J,M)A^{(J')*}_{a\to\bar{a}'+}A^{(J)}_{a\to\bar{a}+}e^{i(\delta_{a\to\bar{a}+}-\delta_{a\to\bar{a}+'})}\ .\end{aligned} \tag{4.12}$$

This result relates the differential cross section to the amplitudes $A^{(J)}_{a\to\bar{a}}$ of the outgoing partial waves of the solution of the TDDF. The terms $P(J,M)$ in Eq. (4.12) are evaluated by inserting $V_q^{\pm}$ for the respective modes of polarization. For linear polarization, we have $V_q^{\pm}=E_0\delta(q,0)$, and for circular polarization $V_q^{\pm}=E_0\delta(q,\pm1)$. In Sec. IV B it is shown how the amplitudes $A^{(J)}_{a\to\bar{a}+}$ can be obtained from the solutions of the homogeneous RRPA equation.

B. Asymptotic amplitudes of the TDDF solutions

To reduce the number of indices, we omit J from $x^{(J)}_{a\to\bar{a}\pm}$ [Eq. (3.15)], assuming that J is fixed. We denote the solutions of the radial *inhomogeneous* equations (3.25) or (3.28) as $x_{a\to\bar{a}\pm}$, and the solutions to the corresponding *homogeneous* equation as $y_{a\to\bar{a}\pm}$. We abbreviate

$$\left[h_{0\bar{a}}-\left[\epsilon_a\pm\begin{Bmatrix}\omega\\2\omega\end{Bmatrix}\right]\right]\equiv\mathcal{L}_{\alpha\to\bar{a}\pm} \tag{4.13}$$

and write for the inhomogeneity in the $a\to\bar{a}$ channel $\mathcal{R}_{\alpha\to\bar{a}}$. Since the central theorem of this section refers to radial integrals, but its proof is much simpler when the equations are not written in angularly decomposed form, we shall write the equations in their original form (2.22), (2.24), inserting the angular expansion (3.15) only for $\mathcal{L}_{\alpha\to\bar{a}\pm}x_{a\to\bar{a}}$ and $\mathcal{R}_{\alpha\to\bar{a}}$, but not for the Coulomb potential terms. The explicit form of the coefficients in Eq. (3.15) has no significance in the context of this section, so we abbreviate

$$\sum_M(-1)^{j_{\bar{a}}-m_{\bar{a}}+J+M}\begin{pmatrix}j_{\bar{a}} & J & j_a\\ -m_{\bar{a}} & -M & m_a\end{pmatrix}P(J,M)\equiv c_{a\to\bar{a}}$$

and imply summation over $\bar{a}$ in all terms that contain $c_{a\to\bar{a}}$, that is, $c_{a\to\bar{a}}x_{a\to\bar{a}\pm}\equiv x_a^{\pm}$. With these abbreviations, the inhomogeneous and homogeneous equations read

$$c_{a\to\bar{a}}\mathcal{L}_{a\to\bar{a}\pm}x_{a\to\bar{a}\pm}+W[u_b,u_b]x_a^{\pm}+(W[x_b^{\mp},u_b]+W[u_b,x_b^{\pm}])u_a+c_{a\to\bar{a}}\mathcal{R}_{a\to\bar{a}\pm}=0\ , \tag{4.14}$$

and

$$c_{a\to\bar{a}}\mathcal{L}_{a\to\bar{a}\pm}y^{(j)}_{a\to\bar{a}\pm}+W[u_b,u_b]y_a^{\pm(j)}+(W[y_b^{\mp(j)},u_b]+W[u_b,y_b^{\pm(j)}])u_a=0\ . \tag{4.15}$$

The solutions decay exponentially for all closed channels. For open channels, they satisfy the asymptotic conditions

$$x_{a\to\bar{a}+}\xrightarrow[r\to\infty]{}A_{a\to\bar{a}+}(\mathsf{c}_{a\to\bar{a}+}+i\mathsf{s}_{a\to\bar{a}+})\quad(a\to\bar{a}\text{ open}) \tag{4.16}$$

and (3.29)

$$y^{(j)}_{a\to\bar{a}+}\xrightarrow[r\to\infty]{}\mathsf{s}_{a\to\bar{a}+}\delta_{a\to\bar{a}+,j}+\mathsf{c}_{a\to\bar{a}+}\mathsf{R}_{a\to\bar{a}+j}\quad(a\to\bar{a}\text{ open})\ . \tag{4.17}$$

Before we continue, let us notice some details pertinent to the following derivation. Equations (4.14) and (4.15) are linear in the positive-frequency and antilinear in the negative-frequency component of the solutions. This will require us to write the Hermitian adjoint of the negative-frequency equations below. $\mathcal{L}_{a\to\bar{a}\pm}$ contains the radial kinetic energy operator $t_{\bar{a}}$ [defined by

$$t_0\frac{1}{r}\begin{pmatrix}is\Omega_{\bar{a}}\\ t\Omega_{-\bar{a}}\end{pmatrix}\equiv\frac{1}{r}t_{\bar{a}}\begin{pmatrix}is\Omega_{-\bar{a}}\\ t\Omega_{\bar{a}}\end{pmatrix}$$

analogous to Eq. (3.6)]

$$t_{\bar{a}}=\begin{pmatrix}0 & \frac{1}{\alpha}\left[\vec{\partial}_r-\frac{\kappa_{\bar{a}}}{r}\right]\\ \frac{1}{\alpha}\left[-\vec{\partial}_r-\frac{\kappa_{\bar{a}}}{r}\right] & 0\end{pmatrix}, \tag{4.18}$$

where $\vec{\partial}$ indicates partial differentiation $\partial/\partial r$ operating to the right. The Hermitian adjoint of this operator is

$$t_{\bar{a}}^{\dagger}=\begin{pmatrix}0 & \frac{1}{\alpha}\left[-\overleftarrow{\partial}_r-\frac{\kappa_{\bar{a}}}{r}\right]\\ \frac{1}{\alpha}\left[\overleftarrow{\partial}_r-\frac{\kappa_{\bar{a}}}{r}\right] & 0\end{pmatrix}. \tag{4.19}$$

Note that the differentiation operates to the left in the adjoint of t. The difference of the operators $t_{\bar{a}}$ and $t_{\bar{a}}^{\dagger}$

$$t_{\bar{a}}-t_{\bar{a}}^{\dagger}=\frac{1}{\alpha}\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}(\vec{\partial}_r+\overleftarrow{\partial}_r)\ , \tag{4.20}$$

sandwiched between the two radial wave functions x and y, yields the derivative of the Wronski determinant of x and y

$$y^{\dagger}(t_{\bar{a}}-t_{\bar{a}}^{\dagger})x=\frac{d}{dr}W(y^*,x)\ . \tag{4.21}$$

Since, at $r=0$, x and y start off proportional to each other, the value of the Wronski determinant at the origin is zero.

We write the positive- and negative-frequency components of Eqs. (4.14), (4.15) separately, taking the adjoint of the *negative*-frequency *inhomogeneous* and *positive*-frequency *homogeneous* equations. Note that $W[u_b,x_b^{\pm}]^{\dagger}=W[x_b^{\pm},u_b]$:

$$
\begin{aligned}
&c_{a\to\bar{a}}\mathcal{L}_{a\to\bar{a}+}x_{a\to\bar{a}+}+W[u_b,u_b]x_a^{+}+(W[x_b^{-},u_b]+W[u_b,x_b^{+}])u_a+c_{a\to\bar{a}}\mathcal{R}_{a\to\bar{a}+}\equiv A_{a\to\bar{a}+}=0\ ,\\
&c_{a\to\bar{a}}x^{\dagger}_{a\to\bar{a}-}\mathcal{L}^{\dagger}_{a\to\bar{a}-}+x_a^{-\dagger}W[u_b,u_b]+u_a^{\dagger}(W[x_b^{-},u_b]+W[u_b,x_b^{+}])+c_{a\to\bar{a}}\mathcal{R}^{\dagger}_{a\to\bar{a}-}\equiv B_{a\to\bar{a}-}=0\ ,\\
&c_{a\to\bar{a}}y^{\dagger}_{a\to\bar{a}+}\mathcal{L}^{\dagger}_{a\to\bar{a}+}+y_a^{+\dagger}W[u_b,u_b]+u_a^{\dagger}(W[y_b^{-},u_b]+W[u_b,y_b^{+}])\equiv C_{a\to\bar{a}+}=0\ ,\\
&c_{a\to\bar{a}}\mathcal{L}_{a\to\bar{a}-}y_{a\to\bar{a}-}+W[u_b,u_b]y_a^{-}+(W[y_b^{-},u_b]+W[u_b,y_b^{+}])u_a\equiv D_{a\to\bar{a}-}=0\ .
\end{aligned}
\tag{4.22}
$$

We form

$$
\int_0^{r_1}dr\int r^2\,d\hat{\mathbf{r}}\,c_{a\to\hat{a}}(y^{\dagger}_{a\to\hat{a}+}A_{a\to\bar{a}+}+B_{a\to\bar{a}-}y_{a\to\hat{a}-}-C_{a\to\bar{a}+}x_{a\to\hat{a}+}-x^{\dagger}_{a\to\hat{a}-}D_{a\to\bar{a}})=0 \tag{4.23}
$$

and observe that the term r^2 cancels with the two factors $1/r$ in the wave functions. The orthonormality relation between spherical spinors induces a factor $\delta_{\bar{a}\hat{a}}$, thus we obtain, after summing over a and letting $r_1\to\infty$, the relation

$$
\begin{aligned}
&\sum_{a,\bar{a}}(c_{a\to\bar{a}})^2\frac{1}{\alpha}[W(y^{*}_{a\to\bar{a}+},x_{a\to\bar{a}+})|_{r=\infty}+W(x^{*}_{a\to\bar{a}-},y_{a\to\bar{a}-})|_{r=\infty}]+\{\cdots\}\\
&\qquad+\sum_{a,\bar{a}}(c_{a\to\bar{a}})^2(\langle y_{a\to\bar{a}+}|\mathcal{R}_{a\to\bar{a}+}\rangle+\langle\mathcal{R}_{a\to\bar{a}-}|y_{a\to\bar{a}-}\rangle)=0\ .
\end{aligned}
\tag{4.24}
$$

The exponential dropoff causes the Wronskians of all closed channels to converge to zero at infinity. Using the orthonormality relation of the 3-j symbols, we can, after summing over m_a and $m_{\bar{a}}$, transform $(c_{a\to\bar{a}})^2$ into $[J]|\sum_M P(J,M)|^2$, which is independent of the summation index and therefore can be factored out of the $(a,\bar{a})$ summation. The terms in ellipses arise from the various components of the Hartree-Fock potential ($W[\,,\,]$) and can easily be shown to cancel, when summed over all orbitals a and b. This yields a relation between radial quantities alone

$$
\begin{aligned}
&\frac{1}{\alpha}\sum_{a\to\bar{a}\in P}W(y^{(j)*}_{a\to\bar{a}+},x_{a\to\bar{a}+})|_{r=\infty}\\
&\qquad+\sum_{a\to\bar{a}}(\langle y^{(j)}_{a\to\bar{a}+}|\mathcal{R}_{a\to\bar{a}+}\rangle+\langle\mathcal{R}_{a\to\bar{a}-}|y^{(j)}_{a\to\bar{a}-}\rangle)=0\ .
\end{aligned}
\tag{4.25}
$$

We finish the derivation by deducing from the asymptotic forms Eqs. (4.16), (4.17), and $W(\mathrm{s,c})=\alpha/\pi$, Eq. (3.11), that

$$
W(y^{(j)*}_{a\to\bar{a}+},x_{a\to\bar{a}+})|_{r=\infty}=A_{a\to\bar{a}+}+\frac{\alpha}{\pi}(\underline{1}-i\underline{R})_{a\to\bar{a},j}\ , \tag{4.26}
$$

which yields, after inverting, the desired final result

$$
\begin{aligned}
A_{a\to\bar{a}+}=-\pi\sum_{b\to\bar{b},j}&(\langle y^{(j)}_{b\to\bar{b}+}|\mathcal{R}_{b\to\bar{b}+}\rangle\\
&+\langle\mathcal{R}_{b\to\bar{b}-}|y^{(j)}_{b\to\bar{b}-}\rangle)[(\underline{1}-i\underline{R})^{-1}]_{j,a\to\bar{a}+}\ .
\end{aligned}
\tag{4.27}
$$

It should be noted that the second-order Lagrange multiplier terms contained in $\mathcal{R}_{a\to\bar{a}\pm}$, which can be determined only by solving the inhomogeneous equation and hence are unknown to us, do not contribute to the integrals in Eq. (4.27) because these terms are proportional to the core orbitals, to which $y^{(j)}_{a\to\bar{a}\pm}$ have been orthogonalized.

C. Results

The numerical procedure to obtain 2PI amplitudes applied in this work is essentially a straightforward extension of Ref. 13. First, the Dirac-Hartree-Fock equation (3.18) is solved for the ground state. The frequencies for 2PI are chosen such that 1PI is energetically impossible and the energy of the final 2PI state is located in the continuum, above the autoionizing range. The first-order TDDF equation (3.25) is solved for these frequencies. A basis set $y^{(j)\pm}_{a\to\bar{a}}$ of the solution space of the homogeneous RRPA equation corresponding to (3.28) with dissociation channels having total angular momentum $J=0$ and 2, and satisfying the asymptotic boundary condition Eq. (3.29), is obtained by an iterative solution process. The details of this procedure are described in Ref. 13. Given the solutions $v_a^{\pm}$ of Eq. (3.25), the inhomogeneity $\mathcal{R}^{\pm}_{a\to\bar{a}}$ [defined in Eq. (4.13)] of Eqs. (2.24) and (3.28) is computed. 2PI amplitudes are determined using the formula Eq. (4.27), and finally, the 2PI cross section is obtained according to Eq. (4.12).

Figures 1–5 show our results for total cross sections of 2PI of the rare gases, both for linear and circular polarization. As a general tendency, the main contributions to the 2PI amplitudes come from the $V^{\pm}|v_a^{\pm}\rangle$ term in the inhomogeneity, whereas the terms containing second-order products of the first-order solutions $v_a^{\pm}$ give only small corrections. This observation was confirmed in a comparison with the results of Starace and Jiang[2] for the special case of argon. The types of correlation corrections included in the TDDF can be obtained by iterating Eqs. (2.22) and (2.24) formally and inserting the iterative solutions into Eq. (4.27). It is found that the formulation of Ref. 2 includes the same type of correlation corrections as ours, at least to lowest-order MBPT. The electron scattering interaction (ESI) level results of Ref. 2 for Ar agree with the present results quantitatively within drawing accuracy.

L'Huillier *et al.* have calculated 2PI cross sections for xenon over a wider energy range in the framework of a nonrelativistic RPA-type approach.[3] Close to threshold,

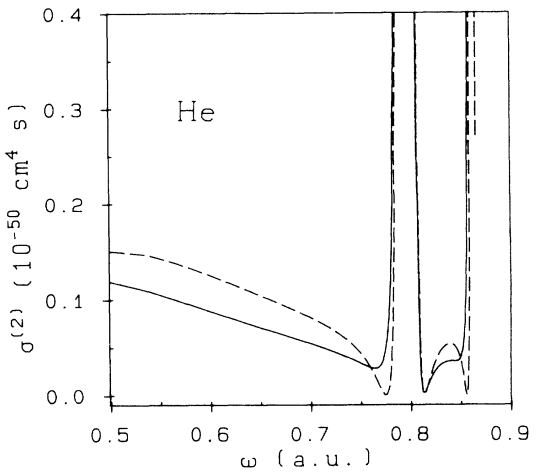

FIG. 1. 2PI total cross section of helium. Abscissa, ω (a.u.). Ordinate, $\sigma^{(2)}$ (10^{-50} cm^{4}s). Solid curve, linear polarization. Dashed curve, circular polarization.

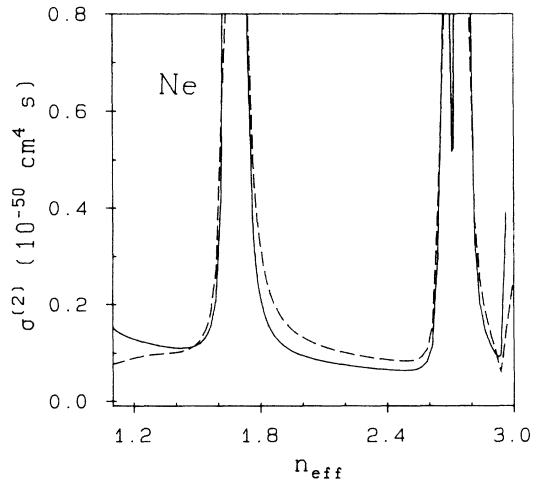

FIG. 2. 2PI total cross section of neon. Abscissa, effective quantum number of intermediate state relative to the $P_{3/2}$ threshold $n_{\text{eff}}=[-1/2(E_{P_{3/2}}+\omega)]^{1/2}$. Ordinate, $\sigma^{(2)}$ (10^{-50} cm^{4}s). Solid curve, linear polarization. Dashed curve, circular polarization.

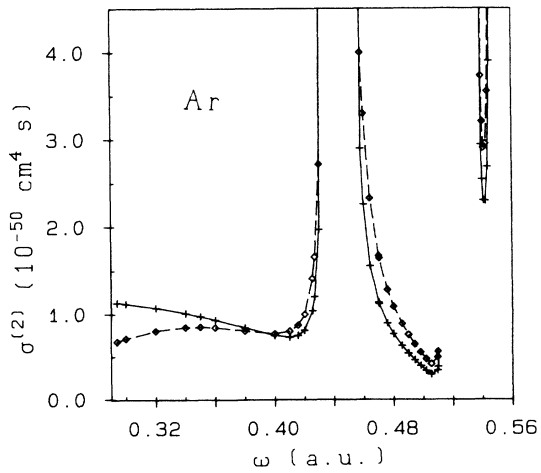

FIG. 3. 2PI total cross section of argon. Abscissa, ω (a.u.). Ordinate, $\sigma^{(2)}$ (10^{-50} cm^{4}s). Data points: +, linear polarization (solid curve); ◇, circular polarization (dashed curve).

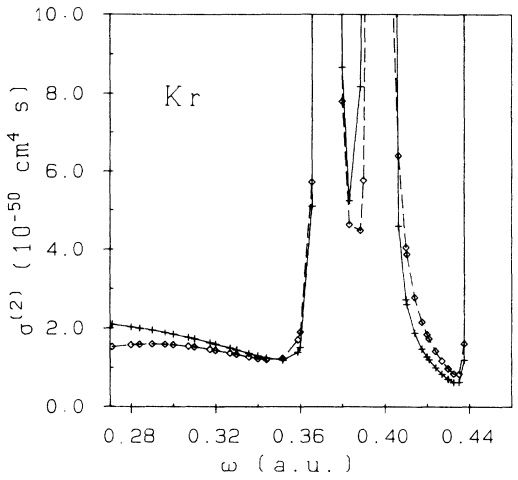

FIG. 4. 2PI total cross section of krypton. Captions as in Fig. 3.

our results are approximately in the middle between the results of Ref. 2 with full screening and with only the first electron-photon interaction screened. As the frequency is increased, our results agree qualitatively with the fully screened results. Due to the pronounced fine structure of xenon, the TDDF approach predicts the positions of the resonances more precisely. In Fig. 6 we show the partial cross sections for 2PI of xenon into the two possible final-state channels leaving behind a $P_{3/2}$ or $P_{1/2}$ Xe^+ core.

The numerical accuracy of the present solutions still needs to be improved. In particular, the iteration procedure to solve the first-order TDDF equation (2.22) converges poorly in the vicinity of resonances. Above the first of first few resonances, it becomes impossible to obtain convergence at all, which is the limiting factor for the frequency ranges treated in the present paper. Our

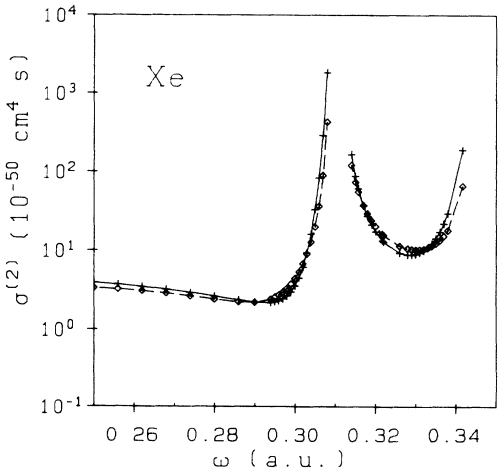

FIG. 5. 2PI total cross section of xenon. Abscissa, ω (a.u.). Ordinate, $\sigma^{(2)}$ (10^{-50} cm^{4}s), logarithmic. Data points: +, linear polarization (solid curve); ◇, circular polarization (dashed curve).

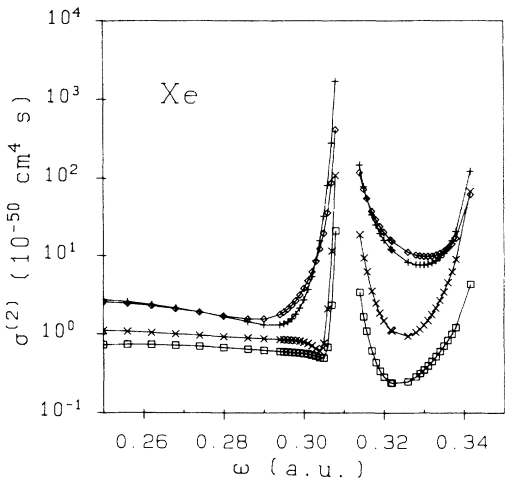

FIG. 6. 2PI partial cross sections of xenon. Abscissa, ω (a.u.). Ordinate, $\sigma^{(2)}$ (10^{-50} cm^{4}s), logarithmic. Data points: +, linear polarization, $P_{3/2}$ final-state core; $\times$ linear polarization, $P_{1/2}$ final-state core; $\Diamond$, circular polarization, $P_{3/2}$ final-state core; $\square$ circular polarization, $P_{1/2}$ final-state core.

numerical results are of a somewhat preliminary character. Inaccuracies of the numerically computed wave functions close to the nucleus, becoming manifest in a failure to obtain exact agreement of the results computed in both length and velocity forms, could not be completely resolved. Theoretically, this agreement should be exact [see the discussion following Eq. (2.13)]. The results reported here are given in length form: The length form of the interaction operator weighs the integrands strongly for large radii and makes the results less sensitive to inaccuracies close the nucleus. For the same reason, truncation of the excitation channels to those arising from the outermost orbitals is only possible in length form. We estimate these results to be numerically more accurate than 5%.

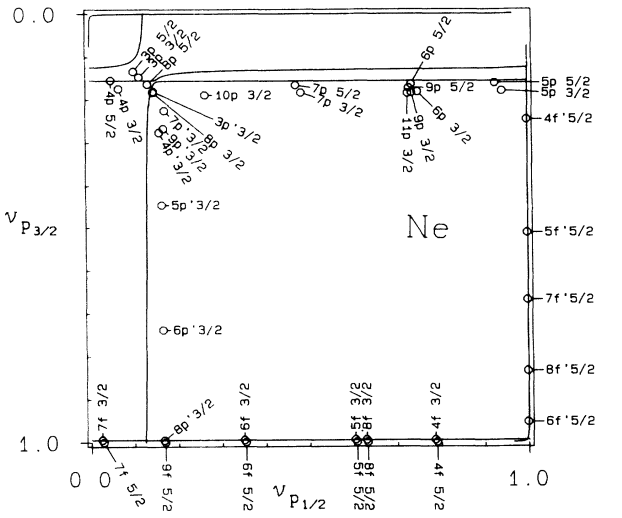

FIG. 8. Lu-Fano MQDT plot for neon $J=2$. Captions as in Fig. 7.

The present approach can be extended to a treatment of two-photon autoionization, that is, 2PI with the final state located energetically between the $P_{3/2}$ and $P_{1/2}$ thresholds of the atom. We have not performed such calculations yet, but the spectral accuracy that is to be expected can be easily assessed from a comparison of the theoretically predicted Lu-Fano MQDT plot[14] with experimental energy levels. In Figs. 7–14, we show the pertinent MQDT plots for the rare gases for total angular momenta $J=0,2$, computed close to threshold. We see that for Ne, the agreement with experiment is excellent; for heavier atoms, it decreases down to the order of 10% of the level spacing in the Rydberg series. A general problem with the TDDF approach is the fact that the

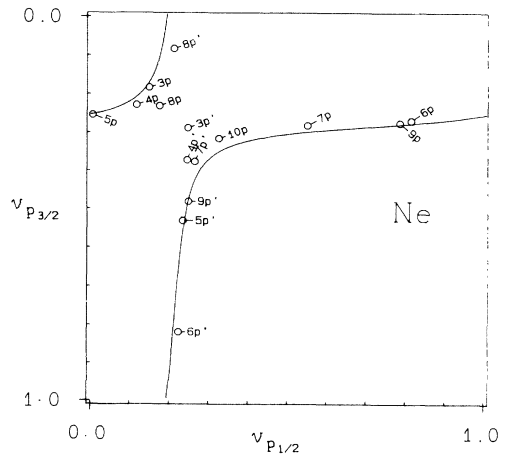

FIG. 7. Lu-Fano MQDT plot for neon $J=0$. Abscissa, $\nu_{P_{1/2}}$. Ordinate, $\nu_{P_{3/2}}$. Solid lines prediction by RRPA reactance matrix. Small circles, experimental levels, with spectral designations.

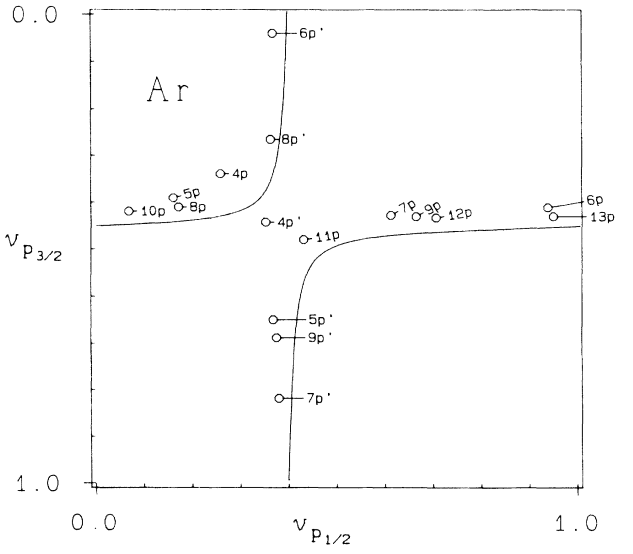

FIG. 9. Lu-Fano MQDT plot for argon $J=0$. Captions as in Fig. 7.

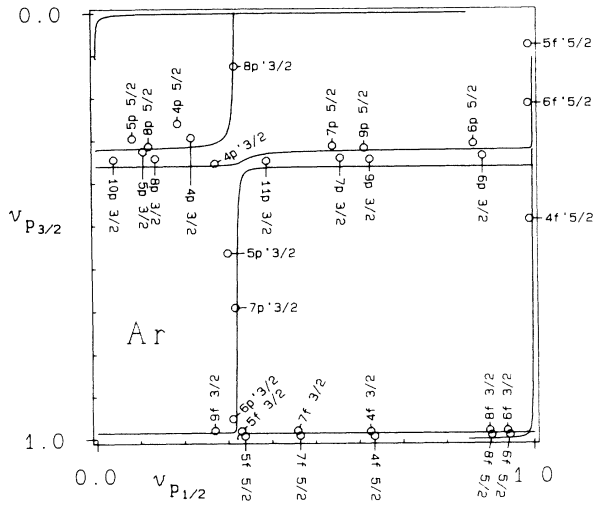

FIG. 10. Lu-Fano MQDT plot for argon $J=2$. Captions as in Fig. 7.

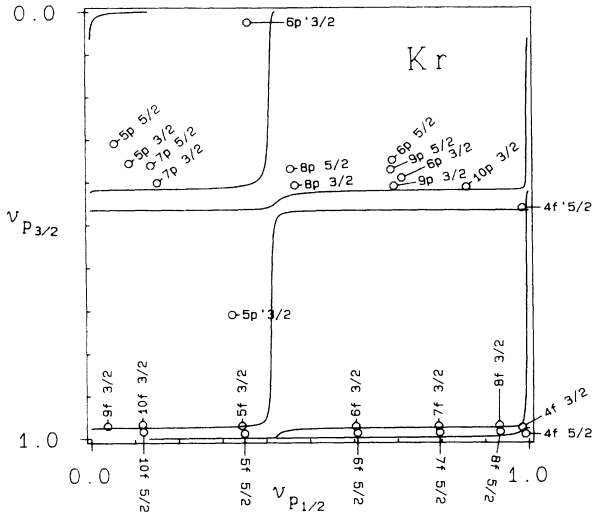

FIG. 12. Lu-Fano MQDT plot for krypton $J=2$. Captions as in Fig. 7.

thresholds predicted by TDDF are identical to the Dirac-Fock binding energies of the respective orbitals (Table I). These thresholds are too high for light atoms, and the fine-structure splitting of the core is generally overestimated. An improvement may be obtained by including higher-order MBPT corrections into the wave functions.

V. CONCLUSIONS

We have formulated a relativistic many-body approach to 2PI of closed-shell atoms that includes both effects of electron correlation and of spin-orbit interaction into 2PI amplitudes. Inclusion of relativistic, and many-body effects makes the TDDF particularly suitable for heavy atoms, where these effects are known to play an important role. Results of numerical evaluations of the equation are given and show good agreement with other computations that account for electron-correlation effects in 2PI. The inclusion of the spin-orbit interaction in the present formulation improves the agreement of the positions of resonances with experiment.

Experiments on one-color two-photon ionization of rare gases from the ground state are most likely to be carried out first for xenon with the final state located in the autoionizing region. An MQDT analysis of autoionizing final-state resonances in the style of Ref. 18 may be one of the most worthwhile extensions of the present work. If experimental necessity arises, angular distributions of photoelectrons, possibly with energy discrimination, can

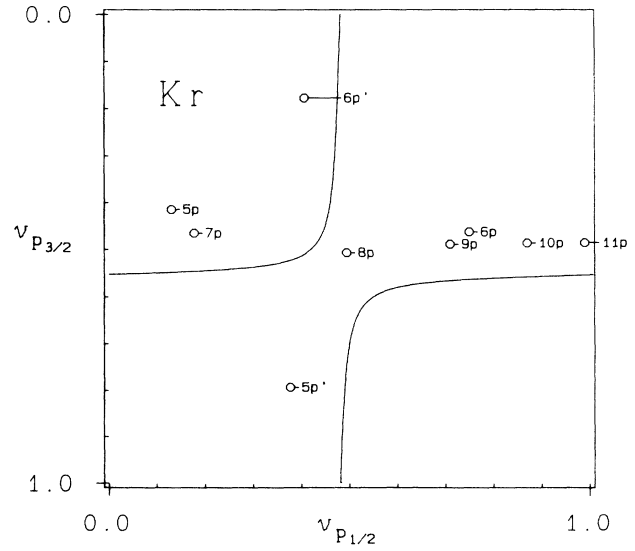

FIG. 11. Lu-Fano MQDT plot for krypton $J=0$. Captions as in Fig. 7.

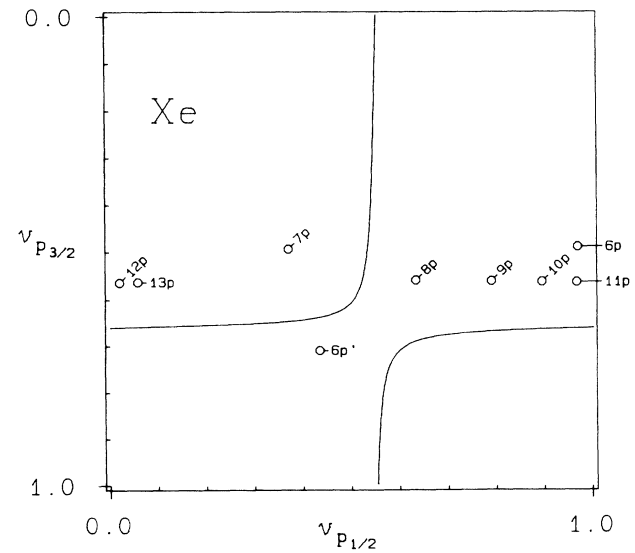

FIG. 13. Lu-Fano MQDT plot for xenon $J=0$. Captions as in Fig. 7.

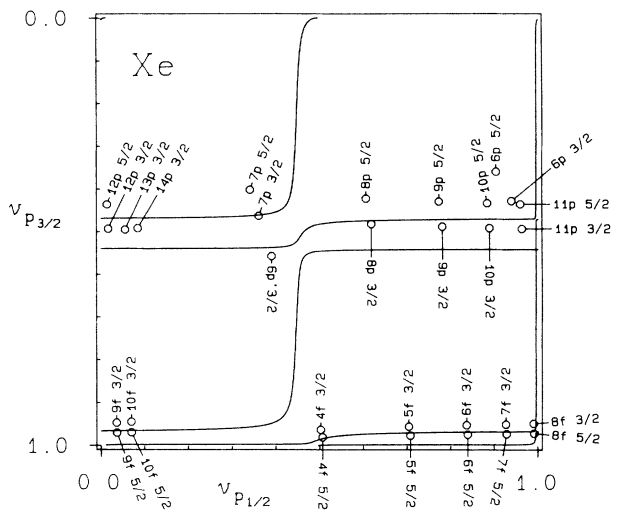

FIG. 14. Lu-Fano MQDT plot for xenon $J=2$. Captions as in Fig. 7.

be obtained for arbitrary polarizations of the exciting field using the formula Eq. (4.12).

The extension of the MQDT parametrization of intermediate resonances in terms of quantities with a smooth energy dependence to TDDF (Ref. 19) is another interesting step, though still academic for the rare gases. It has been pointed out, however, in the treatment of hydrogen, that, although smooth intermediate state wave functions can be found in any case, the existence of physically meaningful smooth matrix elements depends on the transformation of the dipole interaction into a short-range interaction. This still needs to be formulated for relativistic many-body problems.

The TDDF theory can be applied to positive and negative ions in rare-gas configuration. Negative halogen ions appeal by their low binding energy and their strong electron correlation, both caused by the absence of a long-range Coulomb force.

There are two paths to follow when the present method is to be extended to higher orders of MPI. The perturbational expansion of the TDDF equations which we have carried out up to second order in the external field can be continued to arbitrary orders. The main obstacle to a realization of this extension is that the angular reduction results in quite unwieldy radial equations even in the second order [Eq. (3.28)] and becomes almost unmanageable for the third and higher orders. Another possibility is to avoid an order-by-order (in the external field) perturbational expansion of the perturbed orbitals altogether and to make an all-order Floquet expansion of the orbitals in the spirit of Ref. 20. An interesting possibility to improve the accuracy of 2PI amplitudes by variational stabilization of matrix elements was pointed out by Starace *et al.*[21] Incorporating this method into the present context may substantially decrease the computational effort required to obtain 2PI amplitudes of a certain accuracy. As a long term goal, a systematic MBPT approach to MPI needs to be formulated and implemented.

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APPENDIX: MULTIPOLE DECOMPOSITION OF THE COULOMB POTENTIAL

For quantities of angular momentum theory, we use exclusively the conventions and formalism as defined in

TABLE I. Dirac-Fock binding energies for the rare gases. Columns: Element, shell, DF binding energy and $p_{1/2}$-$p_{3/2}$ fine-structure splitting in eV, and experimental spectroscopic binding energy and fine structure in eV.

Element	Shell	DF BE (eV)	FSP (eV)	Expt. BE (eV)	Expt. FSP (eV)
He	$1s$	26.10		24.59	
Ne	$2p_{1/2}$	23.21		21.66	
			0.12		0.10
	$2p_{3/2}$	23.08		21.56	
Ar	$3p_{1/2}$	16.20		15.94	
			0.21		0.18
	$3p_{3/2}$	16.00		15.76	
Kr	$4p_{1/2}$	14.74		14.67	
			0.74		0.67
	$4p_{3/2}$	14.00		14.00	
Xe	$5p_{1/2}$	13.40		13.44	
			1.44		1.31
	$5p_{3/2}$	11.97		12.13	

the book by Lindgren and Morrison.[16] for phase conventions and reduced matrix elements.

The expansion of the Coulomb potential between two electrons with coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ ($r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$) in terms of spherical harmonics C_{LM} is

$$\frac{1}{r_{12}}=\sum_{L,M}\frac{r_<^L}{r_>^{L+1}}(-1)^M C_{LM}(\hat{\mathbf{r}}_1)C_{L-M}(\hat{\mathbf{r}}_2)\ . \tag{A1}$$

We want to decompose the expression $W[s_\alpha,s_\beta]s_\gamma$, where each of the s_i stands for

$$s_i(\hat{\mathbf{r}})=\frac{1}{r}\begin{bmatrix} ig_i(r)\Omega_{\kappa_i m_i}(\hat{\mathbf{r}}) \\ f_i(r)\Omega_{-\kappa_i m_i}(\hat{\mathbf{r}})\end{bmatrix}\ .$$

Defining the relativistic generalization of the radial Hartree screening function

$$\mathcal{R}_L[s_i,s_j](r)\equiv\int dr'\frac{r_<^L}{r_>^{L+1}}[g_i(r')g_j(r')+f_i(r')f_j(r')]\ , \tag{A2}$$

the direct and exchange terms in $W[s_\alpha,s_\beta]s_\gamma$ can each be written in the form

$$\begin{aligned}(\langle s_i|g|s_j\rangle s_k)(\mathbf{r})&\equiv\int d\mathbf{r}'s_i(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}s_j(\mathbf{r}')s_k(\mathbf{r})\\&=\sum_{L,M}\mathcal{R}_L[s_i,s_j](r)(-1)^M\langle\kappa_i m_i|C_{LM}|\kappa_j m_j\rangle\sum_{\kappa_l,m_l}\langle\kappa_l m_l|C_{L-M}|\kappa_k m_k\rangle s_{k:l}\ ,\end{aligned} \tag{A3}$$

where we have made use of the identities $\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\Omega_{\kappa m}=-\Omega_{-\kappa m}$ and $\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}\,\boldsymbol{\sigma}\cdot\hat{\mathbf{r}}=\underline{1}$ and have inserted the completeness relation $\sum_{\kappa,m}\Omega_{\kappa m}\Omega_{\kappa m}^\dagger=\underline{1}$. The symbol $s_{k:l}$ is an abbreviation for a wave function with radial function k and angular dependence l

$$s_{k:l}(\mathbf{r})=\frac{1}{r}\begin{bmatrix} ig_k(r)\Omega_{\kappa_l m_l}(\hat{\mathbf{r}}) \\ f_k(r)\Omega_{-\kappa_l m_l}(\hat{\mathbf{r}})\end{bmatrix}\ . \tag{A4}$$

Carrying out the summation over M, we obtain

$$\langle s_i|g|s_j\rangle s_k=\sum_{L,l,M}\mathcal{R}_L[s_i,s_j](-1)^{M+j_i-m_i+j_l-m_l}\begin{pmatrix} j_i & L & j_j\\ -m_i & -M & m_j\end{pmatrix}\begin{pmatrix} j_l & L & j_k\\ -m_l & M & m_k\end{pmatrix}\langle i\|C_L\|j\rangle\langle l\|C_L\|k\rangle s_{k:l}\ . \tag{A5}$$

Returning to $W[s_\alpha,s_\beta]s_\gamma=\langle s_\alpha|g|s_\beta\rangle s_\gamma-\langle s_\alpha|g|s_\beta\rangle s_\gamma$, we use that for $\alpha,\beta,\gamma,\delta$ half integer the relation

$$\begin{aligned}&\sum_M(-1)^{L+M+j_\alpha-m_\alpha+j_\delta-m_\delta}\begin{pmatrix} j_\alpha & L & j_\gamma\\ -m_\alpha & -M & m_\gamma\end{pmatrix}\begin{pmatrix} j_\delta & L & j_\beta\\ -m_\delta & M & m_\beta\end{pmatrix}\\&\quad=-\sum_{L',M'}[L']\begin{Bmatrix}\alpha&\beta&L'\\ \delta&\gamma&L\end{Bmatrix}(-1)^{L'+M'+j_\alpha-m_\alpha+j_\delta-m_\delta}\begin{pmatrix} j_\alpha & L' & j_\beta\\ -m_\alpha & -M' & m_\beta\end{pmatrix}\begin{pmatrix} j_\delta & L' & j_\gamma\\ -m_\delta & M' & m_\gamma\end{pmatrix}\end{aligned} \tag{A6}$$

can be used to factor out the dependence of both direct and exchange terms on the magnetic quantum numbers. It is convenient to introduce an abbreviation for the product of two reduced matrix elements of C_L and a 6-j symbol

$$A(\alpha\beta,\gamma\delta;LJ)\equiv(-1)^{L+J-j_\beta-j_\gamma}\langle\alpha\|C_L\|\beta\rangle\langle\gamma\|C_L\|\delta\rangle\begin{Bmatrix}\alpha&\beta&L\\ \delta&\gamma&J\end{Bmatrix}\Pi(l_\alpha,l_\gamma,J)\Pi(l_\beta,l_\delta,J)\ , \tag{A7}$$

with the symmetries $A(\alpha\beta,\gamma\delta;LJ)=A(\beta\alpha,\delta\gamma;LJ)=(-1)^{j_\alpha+j_\beta+j_\gamma+j_\delta}A(\gamma\delta,\alpha\beta;LJ)$. Thus $W[s_\alpha,s_\beta]s_\gamma$ finally becomes

$$\begin{aligned}W[s_\alpha,s_\beta]s_\gamma=\sum_{L,J,M,\delta}&(-1)^{L+M+j_\alpha-m_\alpha+j_\delta-m_\delta+J+j_\gamma-j_\delta}\begin{pmatrix} j_\alpha & L & j_\beta\\ -m_\alpha & -M & m_\beta\end{pmatrix}\begin{pmatrix} j_\delta & L & j_\gamma\\ -m_\delta & M & m_\gamma\end{pmatrix}\\&\times\{\delta(L,J)\langle\alpha\|C_L\|\beta\rangle\langle\delta\|C_L\|\gamma\rangle\mathcal{R}_L[s_\alpha,s_\beta]s_{\gamma\cdot\delta}-[J]A(\alpha\gamma,\beta\delta;LJ)\mathcal{R}_L[s_\alpha,s_\gamma]s_{\beta:\delta}\}\ .\end{aligned} \tag{A8}$$

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