Transition matrices for the theory of spectra. Techniques for their construction and calculation*

T. N. Chang† and U. Fano
Department of Physics, University of Chicago, Chicago, Illinois 60637
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Analytical techniques are developed for constructing nth-order (i.e., n-electron) tensor matrices pertaining to transitions of an N-electron atom between two of its stationary states. These matrices serve to calculate the transition amplitude for the atom under the influence of an external field acting on n electrons (typically $n = 1$). Their calculation requires, in turn, the solution of a truncated hierarchy of Schrödinger equations introduced in the preceding paper. The techniques presented here are applied to construct the matrices and their Schrödinger equation for the example of Ar atoms treated in the preceding paper.

I. INTRODUCTION

A recent effort[1] to incorporate the many-body treatments of photoabsorption into the general theory of atomic spectra has stressed the importance of injecting into atomic theory an important element which is characteristic of many-body theories. This is the practice of treating the initial and the final state of a transition simultaneously, concentrating one's attention and computational effort on the differences of their energies and electron distributions, instead of attempting an accurate characterization of either state. The product of the wave function Ψ_a of a stationary state $|a)$ with the wave function Ψ_b^* of another state $|b)$ of an N-electron atom, indicated by

$$\Psi_a\Psi_b^* \equiv (\vec{r}_1, \ldots \vec{r}_i, \ldots \vec{r}_N|a)(b|\vec{r}_1', \ldots \vec{r}_j', \ldots \vec{r}_N') \equiv (\vec{r}_1, \ldots \vec{r}_i, \ldots \vec{r}_N|\Gamma|\vec{r}_1', \ldots \vec{r}_j', \ldots \vec{r}_N'), \quad (1.1)$$

constitutes an element of the space representation of the nonstationary density matrix $|a)(b|$ of the atom. This matrix oscillates with the frequency corresponding to the difference of the two energy levels,

$$E = E_a - E_b . \quad (1.2)$$

In Eq. (1.1) and throughout this paper, $\vec{r}_i$ represents both the position *and spin* of an electron.

We call Γ a transition matrix to distinguish it from the related hierarchy of density matrices introduced by Löwdin[2] for the treatment of a single stationary state. The hierarchy consists of a sequence of nth order reduced matrices

$$(\vec{r}_1 \cdots \vec{r}_n|\Gamma|\vec{r}_1' \cdots \vec{r}_n') = \binom{N}{n}\left(\prod_{i=n+1}^{N}\int\int d\vec{r}_i\, d\vec{r}_i'\,\delta(\vec{r}_i - \vec{r}_i')\right) \times (\vec{r}_1 \cdots \vec{r}_N|\Gamma|\vec{r}_1' \cdots \vec{r}_N'), \quad (1.3)$$

designed to take advantage of the fact that most observable parameters of an atom depend on the positions of a few electrons only (e.g., $n = 1, 2$). Indeed, the definition (1.3) is contrived to facilitate the evaluation of the expectation value of n-electron operators; in the case of $n = 2$, one has

$$O = \sum_{i=1}^{j-1}\sum_{j=2}^{N} O(\vec{r}_i, \vec{r}_j),$$

and

$$\langle O\rangle = \int\int\int\int d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_1'\, d\vec{r}_2'\,[O(\vec{r}_1, \vec{r}_2)(\vec{r}_1, \vec{r}_2|\Gamma|\vec{r}_1', \vec{r}_2')] \times \delta(\vec{r}_1 - \vec{r}_1')\delta(\vec{r}_2 - \vec{r}_2'). \quad (1.4)$$

Given any prescription on the form of the wave functions Ψ_a and Ψ_b, one faces the task of constructing the reduced matrices by Eq. (1.3). A second task consists of constructing and studying the hierarchy of Schrödinger equations

$$[H, \Gamma] = E\Gamma \quad (1.5)$$

integrated over the positions of $N - n$ electrons. These tasks are straightforward in principle, even though complicated. Consequently, Ref. 1 merely presented relevant results without any derivation. It seems worthwhile, however, to discuss the two tasks for their own sake in the present paper and to present a sizable amount of analytical techniques that were developed to simplify and cross check the calculations of Ref. 1. These techniques are variants of existing angular-momentum and density-matrix procedures; they might find extensive applications. Their aim is not only to simplify calculations but also to keep in sight the effects of rotational and other symmetries.

In this broader frame, we mention another point that was touched upon by Ref. 1 but only in a limited context. Much of the theoretical work in spectroscopy has been carried out, whether by many-

body or by traditional methods, in representations using a complete basis of eigenstates of some approximate Hamiltonian. Improved descriptions of phenomena require the admixture of larger portions of this infinite basis. This expansion not only increases the load of computation but also hinders the physical interpretation of the results. By contrast, the approach to be followed here returns to the calculation of wave functions of excited electrons, that is, to the representation in a basis of electron positions. More specifically, it leads to systems of coupled Hartree-Fock radial equations for two or more radial functions, analytically similar to the equations of the close-coupling method. This emphasis on wave equations does not preclude their eventual approximate reduction to algebraic form using an appropriate *finite* basis.

Angular-momentum theory will be utilized systematically, not only for the usual evaluation of angular integrals but also to separate out the spin and angular dependence of transition matrices, much as one separates wave functions in ordinary theory. The resulting simplifications have in fact been carried out at some stage of earlier treatments, but it seems to have been stressed only recently by Rowe and Ngo-Trong[3] that transition matrices or operators separate out into components of different multipolarities. The analytical technique to be used for this purpose will be described in Sec. II.

Antisymmetrization of transition matrices under electron permutations may be achieved, as for wave functions, either by systematic use of antisymmetric Slater determinants, which are then superposed to construct eigenstates of angular momentum, or by applying stepwise procedures in the course of the angular-momentum coupling of orbitals. Use of Slater determinants was predominant in the early development of spectroscopy, and was replaced progressively by alternative procedures. Similarly, we shall find Slater determinants quite convenient to treat the rather simple process of excitation of closed-shell atoms, which has been the object of most applications of many-body theories. Thus, for example, much of the treatment of time-dependent Hartree-Fock and of random-phase procedures in Thouless's book[4] deals with density matrices constructed from a single Slater determinant. We follow this approach here because our immediate goal is to derive formulas used in Ref. 1 for an application to the closed-shell Ar atom. On the other hand, it seems likely that transition matrices of open-shell atoms should be preferably constructed starting from wave functions antisymmetrized by other procedures; we shall introduce this approach in Sec. V.

II. SPIN-ANGULAR MATRICES

Single-electron wave functions are usually factored into a radial part, a spherical function, and a spin function. First-order transition matrices can be similarly expanded into products of radial factors and of spin-angular matrices defined by

$$(l,\hat{r}|w^{[\kappa k]}_{\pi q}|l',\hat{r}') = (-1)^{(1/2)-m'_s}(\tfrac{1}{2}m_s,\tfrac{1}{2}\ -m'_s|\tfrac{1}{2}\tfrac{1}{2}\kappa\pi) \times \sum_{mm'} Y_{lm}(\theta\phi)(-1)^{l'-m'}Y^*_{l'm'}(\theta'\phi') \times (lm, l'-m'|ll'kq). \quad (2.1)$$

As noted in Ref. 1, these w matrices are space representations of double-tensor operators; "double" means that the expression on the right-hand side of Eq. (2.1) represents in compact form the direct product of a spin and of an angular matrix. These matrices represent multipole moments of degree κ and k, respectively, and vanish unless the triads $(\frac{1}{2}\frac{1}{2}\kappa)$ and $(ll'k)$ satisfy the triangular conditions; κ is thus restricted to 0 or 1. The set of all matrices (2.1) with fixed (l,l') is orthonormal in the sense that

$$\int d\hat{r}\int d\hat{r}'\,(l,\hat{r}|w^{[\kappa k]}_{\pi q}|l',\hat{r}')(l,\hat{r}|w^{[\bar{\kappa}\bar{k}]}_{\bar{\pi}\bar{q}}|l',\hat{r}')^* = \delta_{\bar{\kappa}\kappa}\delta_{\bar{k}k}\delta_{\bar{\pi}\pi}\delta_{\bar{q}q}\,. \quad (2.2)$$

(Recall that $\int d\hat{r}$ includes a summation over spin orientation.) A related property is

$$\int d\hat{r}\int d\hat{r}'\,(l,\hat{r}|w^{[\kappa k]}_{\pi q}|l',\hat{r}')(l',\hat{r}'|w^{[\kappa' k']}_{\pi' q'}|l,\hat{r}) = (-1)^{l+l'+\pi+q}\delta_{\kappa\kappa'}\delta_{kk'}\delta_{-\pi\pi'}\delta_{-qq'}\,, \quad (2.3)$$

where the signs stem from the behavior of tensor operators under Hermitian conjugation (see Chap. 14 of Ref. 5). The spin-angular matrices with nonzero values of κ and k are traceless,

$$\int d\hat{r}(l,\hat{r}|w^{[\kappa k]}_{\pi q}|l',\hat{r}) = [\tfrac{1}{2},l]^{1/2}\delta_{\kappa 0}\delta_{k0}\delta_{ll'}\,; \quad (2.4)$$

the symbol $[a,b,\dots]$ means $(2a+1)(2b+1)\cdots$. Irreducible products of spin-angular matrices are constructed by means of Wigner coefficients according to usual conventions, e.g.,

$$[(l_1,\hat{r}_1|w^{[\kappa_1 k_1]}|l'_1,\hat{r}'_1)\times(l_2,\hat{r}_2|w^{[\kappa_2 k_2]}|l'_2,\hat{r}'_2)]^{[\kappa k]}_{\pi q} = \sum_{\pi_1 q_1 \pi_2 q_2}(l_1,\hat{r}_1|w^{[\kappa_1 k_1]}_{\pi_1 q_1}|l'_1,\hat{r}'_1)(l_2,\hat{r}_2|w^{[\kappa_2 k_2]}_{\pi_2 q_2}|l'_2,\hat{r}'_2) \times(\kappa_1\pi_1,\kappa_2\pi_2|\kappa_1\kappa_2\kappa\pi)(k_1q_1,k_2q_2|k_1k_2kq)\,. \quad (2.5)$$

The spin-angular matrices can be treated as operators by integrating over the $\hat{r}$ variable of their products, as in Eq. (2.3). Integrals over simple or multiple tensor products can be eval-

uated in terms of $6j$ or $9j$ coefficients by applying the recoupling procedures of the algebra of tensor operators.[5] The following applications are relevant to this paper.

The scalar operator acts as a unit operator—to within normalization—in that

$$[\tfrac{1}{2}, l]^{1/2}\int d\hat{s}\,(l,\hat{r}|w_{00}^{[00]}|l,\hat{s})(l,\hat{s}|w_{\pi q}^{[\kappa k]}|l',\hat{r}') = [\tfrac{1}{2}, l']^{1/2}\int d\hat{s}\,(l,\hat{r}|w_{\pi q}^{[\kappa k]}|l,\hat{s})(l,\hat{s}|w_{00}^{[00]}|l',\hat{r}') = (l,\hat{r}|w_{\pi q}^{[\kappa k]}|l',\hat{r}'). \quad (2.6)$$

Operation of the first factor of the tensor product (2.5) upon the second factor yields the basic formula

$$\int d\hat{s}\,[(l_1,\hat{r}_1|w^{[\kappa_1 k_1]}|l_1',\hat{s})\times(l_2,\hat{s}|w^{[\kappa_2 k_2]}|l_2',\hat{r}_2')]_{\pi q}^{[\kappa k]} = \delta_{l_2' l_2}(-1)^{l+l_1+l_2'+\kappa+k}[\kappa_1,\kappa_2,k_1,k_2]^{1/2} \times \begin{Bmatrix}\kappa_1 & \kappa_2 & \kappa\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}k_1 & k_2 & k\\ l_2' & l_1 & l_1'\end{Bmatrix}(l_1,\hat{r}_1|w_{\pi q}^{[\kappa k]}|l_2',\hat{r}_2'). \quad (2.7)$$

This result will be used in conjunction with two related recoupling transformations of the algebra of irreducible tensors, namely,

$$w_{\pi q}^{[\kappa k]}[w^{[\kappa' k']}\times w^{[\kappa' k']}]_{00}^{[00]} = \sum_{\kappa'' k''}(-1)^{\kappa+\kappa'-\kappa''+k+k'-k''}[\kappa'',k'']^{1/2}[\kappa,\kappa',k,k']^{-1/2} \times[[w^{[\kappa k]}\times w^{[\kappa' k']}]^{[\kappa'' k'']}\times w^{[\kappa' k']}]_{\pi q}^{[\kappa k]}, \quad (2.8)$$

$$[w^{[\kappa' k']}\times w^{[\kappa' k']}]^{[00]}w_{\pi q}^{[\kappa k]} = \sum_{\kappa'' k''}[\kappa'' k'']^{1/2}[\kappa',\kappa,k',k]^{-1/2} \times[[w^{[\kappa' k']}\times w^{[\kappa k]}]^{[\kappa'' k'']}\times w^{[\kappa' k']}]_{\pi q}^{[\kappa k]}. \quad (2.9)$$

Two other important formulas, which will be employed in Sec. IV, evaluate products of the spin-angular matrices and of the single-tensor operators $C^{[k]}$ which are proportional to the spherical harmonics $Y_{kq}(\hat{r})$,

$$C_q^{[k]}(\hat{r}) = [4\pi/(2k+1)]^{1/2}Y_{kq}(\hat{r}), \quad (2.10)$$

with the reduced matrix element

$$(l'\|C^{[k]}\|l) = (-1)^{l'}[l',l]^{1/2}\begin{pmatrix} l' & k & l\\ 0 & 0 & 0\end{pmatrix}. \quad (2.11)$$

The formulas are

$$[C^{[k]}(\hat{r})\times(l,\hat{r}|w^{[\kappa k_1]}|l',\hat{r}')]^{[\kappa k_2]} = \sum_{\bar{l}}(-1)^{k_2+\bar{l}+l'}[k_1]^{1/2}(\bar{l}\|C^{[k]}\|l)\begin{Bmatrix}\bar{l} & l' & k_2\\ k_1 & k & l\end{Bmatrix} \times(\bar{l},\hat{r}|w^{[\kappa k_2]}|l',\hat{r}') \quad (2.12)$$

and its combination with Eq. (2.4),

$$\int d\hat{r}\,[C^{[k]}(\hat{r})\times(l,\hat{r}|w^{[\kappa k_1]}|l',\hat{r})]^{[\kappa k_2]} = \delta_{\kappa 0}\delta_{k_2 0}\delta_{k_1 k}2^{1/2}(l'\|C^{[k]}\|l). \quad (2.13)$$

III. MATRIX CONSTRUCTION FROM DETERMINANT WAVE FUNCTIONS

In this section we construct transition matrices for the excitation of a closed-shell atom. Since the ground state of this type of atom is represented in zeroth approximation by a single-determinant wave function Ψ_0, it is a simple matter to construct its density matrix Γ_0. Transition matrices are then obtained by applying appropriate excitation operators to Γ_0.

A. Ground-state density matrix

Consider the ground-state wave function in the form $\Psi_0 = (N!)^{-1/2}\,\mathrm{Det}|u_\alpha(\vec{r}_i)|$, where the index $\alpha \equiv (nlmm_s)$ runs over all the N spin orbitals of a sequence of occupied subshells, and $i = 1,2,\ldots N$ as in Sec. I. The complete Nth order density matrix is given, in accordance with Eq. (1.1), by

$$(\vec{r}_1,\ldots\vec{r}_N|\Gamma_0|\vec{r}_1',\ldots\vec{r}_N') = \Psi_0(\cdots\vec{r}_i\cdots)\Psi_0^*(\cdots\vec{r}_i'\cdots) = (N!)^{-1}\,\mathrm{Det}_N\Big|\sum_\alpha u_\alpha(\vec{r}_i)u_\alpha^*(\vec{r}_j')\Big|, \quad (3.1)$$

where the last expression results by matrix multiplication of the determinants in Ψ_0 and Ψ_0^*. We have labeled the product determinant by the subscript N to specify that its row and column indices i and j run from 1 to N. One verifies by stepwise integration, considering the orthonormality of the u_α, that

$$\Big(\prod_{k=n+1}^{N}\int\int d\vec{r}_k\,d\vec{r}_k'\,\delta(\vec{r}_k-\vec{r}_k')\Big)\,\mathrm{Det}_N\Big|\sum_\alpha u_\alpha(\vec{r}_i)u_\alpha^*(\vec{r}_j')\Big| = (N-n)!\,\mathrm{Det}_n\Big|\sum_\alpha u_\alpha(\vec{r}_i)u_\alpha^*(\vec{r}_j')\Big|. \quad (3.2)$$

It follows, by comparison with Eq. (1.3), that the nth-order matrix has the general form

$$(\vec{r}_1,\ldots\vec{r}_n|\Gamma_0|\vec{r}_1',\ldots\vec{r}_n') = (n!)^{-1}\,\mathrm{Det}_n\Big|\sum_\alpha u_\alpha(\vec{r}_i)u_\alpha(\vec{r}_j')\Big|. \quad (3.3)$$

The special case of $n=1$ gives

$$(\vec{r}_1|\Gamma_0|\vec{r}_1') = \sum_\alpha u_\alpha(\vec{r}_1)u_\alpha^*(\vec{r}_1'). \quad (3.4)$$

An extension of this formula serves to represent Eq. (3.3) in the alternative form

$$(\vec{r}_1,\ldots,\vec{r}_n|\Gamma_0|\vec{r}_1',\ldots,\vec{r}_n') = (n!)^{-1}\,\mathrm{Det}_n|(\vec{r}_i|\Gamma_0|\vec{r}_j')|. \quad (3.5)$$

Note the following two properties of the first-order density matrix:

$$\int d\vec{r}_1\,(\vec{r}_1|\Gamma_0|\vec{r}_1)=N, \tag{3.6}$$

$$\int d\vec{s}\,(\vec{r}_1|\Gamma_0|\vec{s})(\vec{s}|\Gamma_0|\vec{r}_1')=(\vec{r}_1|\Gamma_0|\vec{r}_1'). \tag{3.7}$$

The preceding equations are found in textbooks.[4] All of them hold only for states represented by a single-determinant wave function.

When the spin orbitals $u_s(\vec{r})$ of a subshell s are factored into a radial wave function $\chi_s(r)$ and spin-angular factors, the $\sum_\alpha$ extended over the subshell orbitals is represented in terms of a spin-angular matrix by means of Eq. (2.1). Equation (3.4) then takes the form

$$(\vec{r}_1|\Gamma_0|\vec{r}_1')=\sum_s^{\text{occup}}[\tfrac{1}{2},l_s]^{1/2}\chi_s(r_1)(l_s,\hat{r}_1|w_{00}^{[00]}|l_s,\hat{r}_1')\chi_s(r_1'), \tag{3.8}$$

which proves convenient in the following applications.

B. Excitation of a single electron

Consider now the excitation of a single electron from a subshell $s=g$, which is occupied in the ground state, to a subshell of the discrete or continuous spectrum, with orbital momentum l_e. The orbital part of the transition may have any multipolarity k that is consistent with the triangular conditions on $(l_g\,l_e\,k)$, but photoabsorption generally implies $k=1$; the corresponding index κ vanishes in the absence of spin flip or exchange. The transition matrix $\Psi_e(\cdots\vec{r}_i\cdots)\Psi_g^*(\cdots\vec{r}_j'\cdots)$ will thus be a component $T_{\pi q}^{[\kappa k]}$ of a double tensor. The wave function Ψ_e is a superposition of Slater determinants obtained from Ψ_0 by replacing, in turn, each of the wave functions $u_\alpha(\vec{r}_i)$ of its g subshell by a wave function of the excited subshell; the coefficients of the superposition are Wigner coefficients. This construction can be represented compactly in operator language by means of the spin-angular matrices introduced in Sec. II.

We define an elementary single-electron transition matrix

$$(\vec{r}|A|\vec{r}')=\psi_e(r)(l_e,\hat{r}|w_{\pi q}^{[\kappa k]}|l_g,\hat{r}')\chi_g(r'), \tag{3.9}$$

where the radial function $\psi_e(r)$ depends on the excitation level; we also define an operator $\alpha(\vec{r})$ such that

$$\alpha(\vec{r})f(\vec{r})=\int d\vec{s}\,(\vec{r}|A|\vec{s})f(\vec{s}), \tag{3.10}$$

where $f(\vec{r})$ is an arbitrary function. The wave function Ψ_e is then represented by

$$\Psi_e(\cdots\vec{r}_i\cdots)=\sum_{p=1}^{N}\alpha(\vec{r}_p)\Psi_0(\cdots\vec{r}_i\cdots). \tag{3.11}$$

[Note that α actually operates only on the g-subshell columns of Ψ_0 owing to orthogonality to the $u_\alpha(\vec{r}_i)$ of other subshells. Incidentally, no * sign was applied to $\chi_g(r')$ in Eqs. (3.8) and (3.9) because radial functions are real.]

For a fuller study of the excitation from g to e we construct now its transition matrices of various orders, which will be called Γ_1. The full Nth-order transition matrix is simply

$$\begin{aligned}(\vec{r}_1,\ldots\vec{r}_N|\Gamma_1|\vec{r}_1',\ldots\vec{r}_N')&=\Psi_e(\vec{r}_1,\ldots\vec{r}_N)\Psi_g^*(\vec{r}_1',\ldots\vec{r}_N')\\&=\sum_p\alpha(\vec{r}_p)(\vec{r}_1,\ldots\vec{r}_N|\Gamma_0|\vec{r}_1',\ldots\vec{r}_N')\\&=\sum_p\alpha(\vec{r}_p)(N!)^{-1}\,\mathrm{Det}_N|(\vec{r}_i|\Gamma_0|\vec{r}_j')|\,.\end{aligned} \tag{3.12}$$

An important simplification results from the orthonormality of the χ_g factors in the matrix A and the χ_s factors in Eq. (3.8); using also Eq. (2.6), we obtain

$$\alpha(\vec{r}_i)(\vec{r}_i|\Gamma_0|\vec{r}_j')=(\vec{r}_i|A|\vec{r}_j'), \tag{3.13}$$

whereby each term $\alpha(\vec{r}_p)$ in Eq. (3.12) causes the whole pth row of the $\mathrm{Det}_N|(\vec{r}_i|\Gamma_0|\vec{r}_j')|$ to be replaced by $(\vec{r}_p|A|\vec{r}_j')$. Proceeding now to calculate the nth-order matrix by integration, as in Eq. (1.3), we note that the excited orbital in the matrix A is orthogonal to all the ground-state orbitals. Therefore, only the terms of the $\sum_p$ in Eq. (3.12) with $p\leq n$ contribute to the integral. The integration proceeds then as for Γ_0 and yields the general result

$$(\vec{r}_1,\ldots\vec{r}_n|\Gamma_1|\vec{r}_1',\ldots\vec{r}_n')=\sum_{p=1}^{n}\alpha(\vec{r}_p)(n!)^{-1}\,\mathrm{Det}_n|(\vec{r}_i|\Gamma_0|\vec{r}_j')|\,, \tag{3.14}$$

which reduces, for $n=(1,2)$, to

$$(\vec{r}_1|\Gamma_1|\vec{r}_1')=(\vec{r}_1|A|\vec{r}_1'), \tag{3.15}$$

$$(\vec{r}_1\vec{r}_2|\Gamma_1|\vec{r}_1'\vec{r}_2')=\tfrac{1}{2}(1-P_{12})(1-P_{1'2'})(\vec{r}_1|\Gamma_0|\vec{r}_1')(\vec{r}_2|A|\vec{r}_2'). \tag{3.16}$$

Here, and in the following, P_{12} and $P_{1'2'}$ indicate permutation operators for the pairs of variables $(\vec{r}_1,\vec{r}_2)$ and $(\vec{r}_1',\vec{r}_2')$, respectively.

C. Contribution of virtual excitations

The following main aspect of many-body treatments of excitations was discussed and developed in Ref. 1. A consistent treatment of a single-electron excitation requires simultaneous consideration of the virtual excitation of a pair of electrons from the ground state, that is, the ad-

mixture of a doubly excited configuration into the ground-state wave function Ψ_g. The individual orbital quantum numbers of the two excited electrons should have the same value l_e as the excited electron in the state Ψ_e; on the other hand, their combined quantum numbers (L,S) should not change in the course of the virtual excitation owing to angular-momentum conservation. We incorporate this information in the structure of an elementary two-electron transition matrix analogous to the single-electron matrix A defined by Eq. (3.9), namely,

$$(\vec{r}_1\vec{r}_2|B|\vec{r}_1'\vec{r}_2') = \chi_g(r_1)\chi_g(r_2)\sum_{\kappa k}[(l_g,\hat{r}_1|w^{[\kappa k]}|l_e,\hat{r}_1')\times(l_g,\hat{r}_2|w^{[\kappa k]}|l_e,\hat{r}_2')]^{[00]}\, c_{\kappa k}[\varphi_a(r_1')\varphi_b(r_2')+\varphi_b(r_1')\varphi_a(r_2')]. \tag{3.17}$$

The spin-angular factor of this matrix is a scalar, as indicated by [00], which ensures conservation of (S,L), but the multipolarity $[\kappa k]$ of the transition of each electron is unrestricted, at least initially. Altogether, the matrix (3.17) shifts two electrons from the occupied subshell g, with orbital number l_g and radial functions χ_g, to a pair of excited subshells with orbital number l_e and radial functions φ_a and φ_b. The product $\varphi_a\varphi_b$ is symmetrized under permutation of r_1' and r_2' to match the symmetry of $\chi_g(r_1)\chi_g(r_2)$; on the other hand, the spin-angular factor should be antisymmetric under permutations of $(\hat{r}_1,\hat{r}_2)$ as well as of $(\hat{r}_1',\hat{r}_2')$, because the value of $L+S$ for the electron pair is even when in the g subshell and is conserved by the excitation. This antisymmetry requirement restricts the values of the coefficients $c_{\kappa k}$ to those that correspond to electrons paired with even values of $L+S$, and are given by

$$c_{\kappa k} = \sum_{L,S}\tfrac{1}{2}[1+(-1)^{L+S}](-1)^{\kappa+k}[\kappa,k]^{1/2} \times\begin{Bmatrix}\frac{1}{2}&\frac{1}{2}&S\\ \frac{1}{2}&\frac{1}{2}&\kappa\end{Bmatrix}\begin{Bmatrix}l_e&l_e&L\\ l_g&l_g&k\end{Bmatrix} b_{SL}\,; \tag{3.18}$$

the amplitudes b_{SL}, which characterize the parentage of the virtual excitation, remain undetermined. One can verify that the restriction of the sum in Eq. (3.18) to even values of $L+S$ causes the matrix B to be antisymmetric under the permutation P_{12} or $P_{1'2'}$.

These considerations enable us to represent the virtual excitation by operating on the ground-state wave function as indicated by the substitution

$$\Psi_g(\vec{r}_1',\ldots\vec{r}_N')\rightarrow\Psi_g(\vec{r}_1',\ldots\vec{r}_N')\Big(1+\sum_{u=1}^{v-1}\sum_{v=2}^{N}\beta(\vec{r}_u',\vec{r}_v')\Big), \tag{3.19}$$

where the two-electron symbol β operates as α does in Eq. (3.10),

$$f(\vec{r}_1',\vec{r}_2')\,\beta(\vec{r}_1',\vec{r}_2') = \int\int d\vec{r}\,d\vec{s}\, f(\vec{r},\vec{s})(\vec{r}\vec{s}|B|\vec{r}_1'\vec{r}_2'). \tag{3.20}$$

This same operation changes the Nth-order transition matrix (3.12) into

$$\Psi_e(\vec{r}_1,\ldots\vec{r}_N)\Psi_g^*(\vec{r}_1',\ldots\vec{r}_N')\Big(1+\sum_{u=1}^{v-1}\sum_{v=2}^{N}\beta(\vec{r}_u',\vec{r}_v')\Big) = (\vec{r}_1,\ldots\vec{r}_N|\Gamma_1|\vec{r}_1',\ldots\vec{r}_N')+(\vec{r}_1,\ldots\vec{r}_N|\Gamma_2|\vec{r}_1',\ldots\vec{r}_N'), \tag{3.21}$$

where Γ_1 is given by (3.12), and

$$(\vec{r}_1,\ldots\vec{r}_N|\Gamma_2|\vec{r}_1',\ldots\vec{r}_N') = \sum_{p=1}^{N}\alpha(\vec{r}_p)(N!)^{-1}\,\mathrm{Det}_N|(\vec{r}_i|\Gamma_0|\vec{r}_j')|\sum_{u=1}^{v-1}\sum_{v=2}^{N}\beta(\vec{r}_u',\vec{r}_v'). \tag{3.22}$$

When calculating lower-order matrices by multiple integration, as in Eq. (1.3), one should consider that the excited orbitals reached by the operators α and β are orthogonal to all the ground-state orbitals but are not mutually orthogonal. Consequently only a subset of all terms of Eq. (3.22) contributes to the integral. In the simplest case of the first-order transition matrix, the subset consists of the terms with $u=1$ and $p=v>1$. Further, since all terms with $v=2,3,\ldots N$ contribute equally, we may set $p=v=2$ and multiply the result by $N-1$. The integration over all the variables with $i>2$ is then given by (3.2), and we find

$$(\vec{r}_1|\Gamma_2|\vec{r}_1') = \int\int d\vec{r}_2\,d\vec{r}_2'\,\delta(\vec{r}_2-\vec{r}_2') \times[\alpha(\vec{r}_2)\,\mathrm{Det}_2|(\vec{r}_i|\Gamma_0|\vec{r}_j')|\beta(\vec{r}_1',\vec{r}_2')]. \tag{3.23}$$

The considerations that led to Eq. (3.13) now yield

$$\mathrm{Det}_2|(\vec{r}_i|\Gamma_0|\vec{r}_j')|\beta(\vec{r}_1',\vec{r}_2') = (\vec{r}_1\vec{r}_2|B|\vec{r}_1'\vec{r}_2')-(\vec{r}_2\vec{r}_1|B|\vec{r}_1'\vec{r}_2') = 2(\vec{r}_1\vec{r}_2|B|\vec{r}_1'\vec{r}_2'), \tag{3.24}$$

owing to antisymmetry of B under P_{12}. Equation (3.23) thus reduces to

$$(\vec{r}_1|\Gamma_2|\vec{r}_1') = 2\int\int d\vec{r}\,d\vec{s}\,(\vec{r}|A|\vec{s})(\vec{r}_1\vec{s}|B|\vec{r}_1'\vec{r}). \tag{3.25}$$

The radial integral over s, in this equation, is $\int_0^\infty \chi_g(s)^2\,ds = 1$; the integration over r yields a superposition of φ_a and φ_b which we call

$$\phi(r_1') = \Big(\varphi_a(r_1')\int_0^\infty \varphi_b(r)\psi(r)\,dr + \varphi_b(r_1')\int_0^\infty \varphi_a(r)\psi(r)\,dr\Big) \times (-1)^{l_g+l_e+\kappa+k}\,2[\kappa,k]^{-1/2}c_{\kappa k}. \tag{3.26}$$

The spin-angular integrations proceed by successive application of Eqs. (2.6), (2.7), and (2.8), and the final form of Eq. (3.25) is

$$(\vec{r}_1|\,\Gamma_2|\,\vec{r}_1') = \chi_g(r_1)(l_g\,\hat{r}_1|w^{[\kappa k]}_{\pi q}|\,l_e\,\hat{r}_1')\phi(r_1'). \tag{3.27}$$

Remarkably, as noted in Ref. 1, the occurrence of virtual excitations of *two* electrons, to states with radial functions φ_a and φ_b, contributes a first-order matrix equivalent to the deexcitation of a *single* electron from a radial orbital ϕ.

Proceeding finally to the evaluation of the second-order matrix Γ_2, we notice that the multiple integral with $i>2$ receives nonvanishing contributions only from two groups of terms of Eq. (3.22). The first contribution, to be called Γ_{2a}, stems from $p=1$ or 2, with $u=1$ and $v=2$, while the second, to be called Γ_{2b}, stems from $u=1$ or 2, with $p=v>2$. For Γ_{2a} the integrations over r_k are now given by Eq. (3.2) and yield

$$(\vec{r}_1\vec{r}_2|\,\Gamma_{2a}|\,\vec{r}_1'\vec{r}_2') = [\alpha(\vec{r}_1)+\alpha(\vec{r}_2)]\tfrac{1}{2}\,\mathrm{Det}_2|(\vec{r}_i|\,\Gamma_0|\,\vec{r}_j')|\,\beta(\vec{r}_1',\vec{r}_2') = [\alpha(\vec{r}_1)+\alpha(\vec{r}_2)](\vec{r}_1\vec{r}_2|B|\vec{r}_1'\vec{r}_2')$$

$$= (1-P_{12})\int d\vec{s}\,(\vec{r}_1|A|\vec{s})(\vec{s}\vec{r}_2|B|\vec{r}_1'\vec{r}_2')$$

$$= (1+P_{12}P_{1'2'})\Big(\sum_{\kappa''k''\kappa'k'}(-1)^{1+\kappa''+k''}[\kappa'',k'']^{1/2}\begin{Bmatrix}\kappa & \kappa'' & \kappa'\\ \frac12 & \frac12 & \frac12\end{Bmatrix}\begin{Bmatrix}k & k'' & k'\\ l_e & l_g & l_e\end{Bmatrix}c_{\kappa'k'}$$

$$\times\psi_e(r_1)\chi_g(r_2)[(l_e\hat{r}_1|w^{[\kappa''k'']}|\,l_e\hat{r}_1')\times(l_g\hat{r}_2|w^{[\kappa'k']}|\,l_e\hat{r}_2')]^{[\kappa k]}_{\pi q}[\varphi_a(r_1')\varphi_b(r_2')+\varphi_b(r_1')\varphi_a(r_2')]\Big). \tag{3.28}$$

Here the antisymmetry of B has served to replace the term $\alpha(\vec{r}_2)$ by the factor $1+P_{12}P_{1'2'}$, and the spin-angular integral has been evaluated by Eqs. (2.7) and (2.8).

In the evaluation of Γ_{2b} only the integrations over $\vec{r}_i$ with $i>3$ can be done by Eq. (3.2), yielding

$$(\vec{r}_1\vec{r}_2|\,\Gamma_{2b}|\,\vec{r}_1'\vec{r}_2') = \tfrac{1}{2}\int\int d\vec{r}_3\,d\vec{r}_3'\,\delta(\vec{r}_3-\vec{r}_3')\{\alpha(\vec{r}_3)\,\mathrm{Det}_3|(\vec{r}_i|\,\Gamma_0|\,\vec{r}_j')|\,[\beta(\vec{r}_1',\vec{r}_3')+\beta(\vec{r}_2',\vec{r}_3')]\}. \tag{3.29}$$

The determinant in this equation has the suitable expansion

$$\mathrm{Det}_3|(\vec{r}_i|\,\Gamma_0|\,\vec{r}_j')| = (1-P_{12})(\vec{r}_1|\,\Gamma_0|\,\vec{r}_1')\begin{vmatrix}(\vec{r}_2|\,\Gamma_0|\,\vec{r}_2') & (\vec{r}_2|\,\Gamma_0|\,\vec{r}_3')\\ (\vec{r}_3|\,\Gamma_0|\,\vec{r}_2') & (\vec{r}_3|\,\Gamma_0|\,\vec{r}_3')\end{vmatrix} + (\vec{r}_3|\,\Gamma_0|\,\vec{r}_1')\begin{vmatrix}(\vec{r}_1|\,\Gamma_0|\,\vec{r}_2') & (\vec{r}_1|\,\Gamma_0|\,\vec{r}_3')\\ (\vec{r}_2|\,\Gamma_0|\,\vec{r}_2') & (\vec{r}_2|\,\Gamma_0|\,\vec{r}_3')\end{vmatrix}. \tag{3.30}$$

The expression inside the curly brackets of Eq. (3.29) can be improved by inserting a factor $1-P_{1'2'}$, i.e.,

$$\alpha(\vec{r}_3)\,\mathrm{Det}_3|(\vec{r}_i|\,\Gamma_0|\,\vec{r}_j')|\,[\beta(\vec{r}_1',\vec{r}_3')+\beta(\vec{r}_2',\vec{r}_3')] = \alpha(\vec{r}_3)(1-P_{1'2'})\,\mathrm{Det}_3|(\vec{r}_i|\,\Gamma_0|\,\vec{r}_j')|\,\beta(\vec{r}_2',\vec{r}_3'). \tag{3.31}$$

The effect of $\beta(r_2',r_3')$ itself upon Eq. (3.30) is, according to Eq. (3.24),

$$\tfrac{1}{2}\,\mathrm{Det}_3|(\vec{r}_i|\,\Gamma_0|\,\vec{r}_j')|\,\beta(\vec{r}_2',\vec{r}_3') = (1-P_{12})(\vec{r}_1|\,\Gamma_0|\,\vec{r}_1')(\vec{r}_2\vec{r}_3|B|\vec{r}_2'\vec{r}_3') + (\vec{r}_3|\,\Gamma_0|\,\vec{r}_1')(\vec{r}_1\vec{r}_2|B|\vec{r}_2'\vec{r}_3'). \tag{3.32}$$

There remains to apply the operator $\alpha(\vec{r}_3)(1-P_{1'2'})$ on the left-hand side of this expression and to carry out the integral (replacing $\vec{r}_3$ by $\vec{t}$) in Eq. (3.29). According to Eqs. (3.10) and (3.13), the result is

$$(\vec{r}_1\vec{r}_2|\,\Gamma_{2b}|\,\vec{r}_1'\vec{r}_2') = (1-P_{12})(1-P_{1'2'})(\vec{r}_1|\,\Gamma_0|\,\vec{r}_1)\int\int d\vec{t}\,d\vec{s}\,(\vec{t}|A|\vec{s})(\vec{r}_2\vec{s}|B|\vec{r}_2'\vec{t}) + (1-P_{1'2'})\int d\vec{t}\,(\vec{r}_1\vec{r}_2|B|\vec{r}_2'\vec{t})(\vec{t}|A|\vec{r}_1'). \tag{3.33}$$

The first integral on the right-hand side of this expression is provided by Eqs. (3.25) and (3.27); the second one, analogous to that in Eq. (3.28), is found to be

$$(1-P_{1'2'})\int d\vec{t}\,(\vec{r}_1\vec{r}_2|B|\vec{r}_2'\vec{t})(\vec{t}|A|\vec{r}_1')$$

$$= \frac{1+P_{12}P_{1'2'}}{2}\sum_{\kappa'k'\kappa''k''}(-1)^{l_g+l_e+\kappa'+k'}[\kappa,\kappa'',k,k'']^{1/2}\begin{Bmatrix}\kappa & \kappa'' & \kappa'\\ \frac12 & \frac12 & \frac12\end{Bmatrix}\begin{Bmatrix}k & k'' & k'\\ l_g & l_e & l_g\end{Bmatrix}\frac{c_{\kappa'k'}}{c_{\kappa k}}$$

$$\times\chi_g(r_1)\phi(r_1')[(l_g,\hat{r}_1|w^{[\kappa'k']}|\,l_e,\hat{r}_1')\times(l_g,\hat{r}_2|w^{[\kappa''k'']}|\,l_g,\hat{r}_2')]^{[\kappa k]}_{\pi q}\chi_g(r_1')\chi_g(r_2'). \tag{3.34}$$

D. The combined transition matrix

We combine here the first- and second-order matrices obtained from the two terms of the Nth-order matrix, Eq. (3.21). The first-order matrix derived from Γ_1 is given by Eqs. (3.15) and (3.9); the one derived from Γ_2 is given by Eq. (3.27). Their sum is

$$(\vec{r}_1|\Gamma|\vec{r}_1') = \psi_e(r_1)(l_e,\hat{r}_1|w_{\pi q}^{[\kappa k]}|l_g,\hat{r}_1')\chi_g(r_1') + \chi_g(r_1)(l_g,\hat{r}_1|w_{\pi q}^{[\kappa k]}|l_e,\hat{r}_1')\phi(r_1'). \tag{3.35}$$

With regard to the second-order matrix, we begin by noticing that both the contribution of Γ_1 and the first term on the right-hand side of Eq. (3.33) consist of one factor $(\vec{r}_1|\Gamma_0|\vec{r}_1')$ and one factor which is included in the first-order matrix (3.35). Their combined contribution is then represented simply by

$$\tfrac{1}{2}(1-P_{12})(1-P_{1'2'})(\vec{r}_1|\Gamma_0|\vec{r}_1')(\vec{r}_2|\Gamma|\vec{r}_2').$$

The remaining contributions are then represented by Eq. (3.28) and by the second term on the right-hand side of Eq. (3.33), whose explicit form is given by Eq. (3.34). Adding these three contributions we obtain

$$\begin{aligned}(\vec{r}_1,\vec{r}_2|\Gamma|\vec{r}_1',\vec{r}_2') &= \tfrac{1}{2}(1-P_{12})(1-P_{1'2'})(\vec{r}_1|\Gamma_0|\vec{r}_1')(\vec{r}_2|\Gamma|\vec{r}_2')\\
&+\tfrac{1}{2}(1+P_{12}P_{1'2'})\sum_{\kappa' k' \kappa'' k''}(-1)^{l_g+l_e+\kappa'+k'}[\kappa,\kappa'',k,k'']^{1/2}\begin{Bmatrix}\kappa & \kappa'' & \kappa'\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}k & k'' & k'\\ l_g & l_e & l_g\end{Bmatrix}\frac{c_{\kappa' k'}}{c_{\kappa k}}\chi_g(r_1)\chi_g(r_2)\\
&\times[(l_g,\hat{r}_1|w^{[\kappa' k']}|l_e,\hat{r}_1')\times(l_g,\hat{r}_2|w^{[\kappa'' k'']}|l_g,\hat{r}_2')]_{\pi q}^{[\kappa k]}\phi(r_1')\chi_g(r_2')\\
&+\tfrac{1}{2}(1+P_{12}P_{1'2'})\sum_{\kappa' k' \kappa'' k''}(-1)^{1+\kappa''+k''}[\kappa'',k'']^{1/2}\begin{Bmatrix}\kappa & \kappa'' & \kappa'\\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}k & k'' & k'\\ l_e & l_g & l_e\end{Bmatrix}c_{\kappa' k'}\psi_e(r_1)\chi_g(r_2)\\
&\times[(l_e,\hat{r}_1|w^{[\kappa'' k'']}|l_e,\hat{r}_1')\times(l_g,\hat{r}_2|w^{[\kappa' k']}|l_e,\hat{r}_2')]_{\pi q}^{[\kappa k]}[\varphi_a(r_1')\varphi_b(r_2')+\varphi_a(r_2')\varphi_b(r_1')].\end{aligned} \tag{3.36}$$

This result reduces, for the example of Ar, to Eq. (24) of Ref. 1 by setting $\kappa=0$, $k=1$, $\pi=0$, $q=0$, $g=3p$, $l_g=1$, and $l_e=2$.

IV. CONSTRUCTION OF THE SCHRÖDINGER EQUATION FOR THE FIRST-ORDER TRANSITION MATRIX

Consider initially the general program of integrating the N-particle Schrödinger equation (1.5) over the coordinates of $N-n$ electrons as indicated in Eq. (1.3). The Hamiltonian has the form

$$H = \sum_i H_0(\vec{r}_i) + \sum_{i<j}|\vec{r}_i - \vec{r}_j|^{-1}, \tag{4.1}$$

where H_0 is the sum of the single-particle kinetic energy operator and the attractive Coulomb potential that is due to the nuclear charge Z, and the two-particle operator $|\vec{r}_i-\vec{r}_j|^{-1}$ represents the repulsive Coulomb interaction between two atomic electrons. The contributions of the terms $\sum_{i=n+1}^{N}H_0(\vec{r}_i)$ operating on the two sides of Γ cancel because H_0 is Hermitian. The terms $\sum_{i=1}^{n}H_0(\vec{r}_i)$ remain as operators on the nth-order matrix. Similarly, the terms of $\sum_{i<j}|\vec{r}_i-\vec{r}_j|^{-1}$ with $i>n$ yield no net contribution, while those with $j\leq n$ remain as operators on the nth-order matrix. The nontrivial terms are those with $i\leq n$ and $j>n$. For any given $i\leq n$, identical contributions result from the $N-n$ values of $j>n$. These terms can be condensed in the form

$$\begin{aligned}(n+1)\binom{N}{n}^{-1}\int\int d\vec{r}_{n+1}\,d\vec{r}_{n+1}'\,\delta(\vec{r}_{n+1}-\vec{r}_{n+1}')\\
\times\sum_{i=1}^{N}(|\vec{r}_i-\vec{r}_{n+1}|^{-1}-|\vec{r}_i'-\vec{r}_{n+1}'|^{-1})\\
\times(\vec{r}_1,\ldots\vec{r}_{n+1}|\Gamma|\vec{r}_1',\ldots\vec{r}_{n+1}').\end{aligned} \tag{4.2}$$

Thus we obtain the essential point raised in Ref. 1, that the equation for the nth-order matrix involves integration over the matrix of $(n+1)$st order,

$$\begin{aligned}&\sum_{p=1}^{n}[H_0(\vec{r}_p)(\vec{r}_1,\ldots\vec{r}_n|\Gamma|\vec{r}_1',\ldots\vec{r}_n') - (\vec{r}_1,\ldots\vec{r}_n|\Gamma|\vec{r}_1',\ldots\vec{r}_n')H_0(\vec{r}_p')]\\
&+\sum_{u=1}^{v-1}\sum_{v=2}^{n}(|\vec{r}_u-\vec{r}_v|^{-1}-|\vec{r}_u'-\vec{r}_v'|^{-1})(\vec{r}_1,\ldots\vec{r}_n|\Gamma|\vec{r}_1',\ldots\vec{r}_n')\\
&+(n+1)\int\int d\vec{r}_{n+1}\,d\vec{r}_{n+1}'\,\delta(\vec{r}_{n+1}-\vec{r}_{n+1}')\sum_{p=1}^{n}(|\vec{r}_p-\vec{r}_{n+1}|^{-1}-|\vec{r}_p'-\vec{r}_{n+1}'|^{-1})(\vec{r}_1,\ldots\vec{r}_{n+1}|\Gamma|\vec{r}_1',\ldots\vec{r}_{n+1}')\\
&=E(\vec{r}_1,\ldots\vec{r}_n|\Gamma|\vec{r}_1',\ldots\vec{r}_n').\end{aligned} \tag{4.3}$$

For the case relevant to Ref. 1, namely, for the first-order matrix ($n=1$), Eq. (4.3) takes the form

$$H_0(r_1)(\vec{r}_1|\Gamma|\vec{r}_1') - (\vec{r}_1|\Gamma|\vec{r}_1')H_0(r_1') + 2\int\int d\vec{r}_2\, d\vec{r}_2'\,\delta(\vec{r}_2-\vec{r}_2')[(|\vec{r}_1-\vec{r}_2|^{-1}-|\vec{r}_1'-\vec{r}_2'|^{-1})(\vec{r}_1,\vec{r}_2|\Gamma|\vec{r}_1',\vec{r}_2')] = E(\vec{r}_1|\Gamma|\vec{r}_1'), \tag{4.4}$$

where

$$H_0(r_1) = \sum_i \left(-\frac{1}{2}\frac{d^2}{dr_1^2} - \frac{Z}{r_1} + \frac{1}{2}\frac{l(l+1)}{r_1^2}\right), \tag{4.5}$$

and $(\vec{r}_1|\Gamma|\vec{r}_1')$ and $(\vec{r}_1,\vec{r}_2|\Gamma|\vec{r}_1',\vec{r}_2')$ are the first- and second-order transition matrices given by Eqs. (3.35) and (3.36), respectively. In the rest of this section we shall concentrate our effort on the evaluation of the integral term in Eq. (4.4).

To calculate the term

$$2\int\int d\vec{r}_2\, d\vec{r}_2'\,\delta(\vec{r}_2-\vec{r}_2')[(|\vec{r}_1-\vec{r}_2|^{-1}-|\vec{r}_1'-\vec{r}_2'|^{-1})(\vec{r}_1,\vec{r}_2|\Gamma|\vec{r}_1',\vec{r}_2')], \tag{4.6}$$

we first expand $|\vec{r}_1-\vec{r}_2|^{-1}$ into Legendre polynomials $P_k(\hat{r}_1\cdot\hat{r}_2)$ which are in turn to be represented as the products of two tensor operators $C^{[k]}$ given in Eq. (2.10):

$$|\vec{r}_1-\vec{r}_2|^{-1} = \sum_{k=0}^{\infty}\frac{r_<^k}{r_>^{k+1}}P_k(\hat{r}_1\cdot\hat{r}_2) = \sum_{k=0}^{\infty}\frac{r_<^k}{r_>^{k+1}}(-1)^k[k]^{1/2}[C^{[k]}(\hat{r}_1)\times C^{[k]}(\hat{r}_2)]^{[0]}. \tag{4.7}$$

The radial integration of Eq. (4.6) is straightforward; we return to it below. The spin-angular integration takes various forms related to the permutations of coordinates P_{12} and $P_{1'2'}$ in $(\vec{r}_1,\vec{r}_2|\Gamma|\vec{r}_1',\vec{r}_2')$.

We proceed by first considering the two spin-angular integrals which are relevant to the case discussed in Ref. 1,

$$J_k(l_1\,l_2,\,l_1'l_2';\,\kappa k_1k_2) = \int\int d\hat{r}_2\, d\hat{r}_2'\,\delta(\hat{r}_2-\hat{r}_2')P_k(\hat{r}_1\cdot\hat{r}_2)[(l_1,\hat{r}_1|w^{[\kappa k_1]}|l_1',\hat{r}_1')\times(l_2,\hat{r}_2|w^{[\kappa k_2]}|l_2',\hat{r}_2')]_{00}^{[01]} \tag{4.8a}$$

and

$$J_k'(l_1l_2,\,l_1'l_2';\,\kappa k_1k_2) = \int\int d\hat{r}_2\, d\hat{r}_2'\,\delta(\hat{r}_2-\hat{r}_2')[(l_1,\hat{r}_1|w^{[\kappa k_1]}|l_1',\hat{r}_1')\times(l_2,\hat{r}_2|w^{[\kappa k_2]}|l_2',\hat{r}_2')]_{00}^{[01]}P_k(\hat{r}_1'\cdot\hat{r}_2'). \tag{4.8b}$$

To carry out the integration, we recall that $P_k(\hat{r}_1\cdot\hat{r}_2)\propto[C^{[k]}(\hat{r}_1)\times C^{[k]}(\hat{r}_2)]^{[0]}$, and we rearrange the coupling in such a way that the operator $C^{[k]}(\hat{r}_1)$ is coupled with the spin-angular matrix $(l_1,\hat{r}_1|w^{[\kappa k_1]}|l_1',\hat{r}_1')$ and $C^{[k]}(\hat{r}_2)$ with $(l_2,\hat{r}_2|w^{[\kappa k_2]}|l_2',\hat{r}_2')$, i.e.,

$$J_k = (-1)^k[k]^{1/2}\sum_{j_1j_2}((kk_1)j_1,\,(kk_2)j_2,\,1|(kk)0,\,(k_1k_2)1,\,1)\int d\hat{r}_2[[C^{[k]}(\hat{r}_1)\times(l_1,\hat{r}_1|w^{[\kappa k_1]}|l_1',\hat{r}_1')]^{[\kappa j_1]} \times[C^{[k]}(\hat{r}_2)\times(l_2,\hat{r}_2|w^{[\kappa k_2]}|l_2',\hat{r}_2)]^{[\kappa j_2]}]_{00}^{[01]}, \tag{4.9}$$

using the standard expression for the recoupling coefficient.[6] This integral can be readily evaluated by applying Eqs. (2.12) and (2.13):

$$\begin{aligned} J_k &= \delta_{\kappa 0}\delta_{k_2k}(-1)^{1+k_1}[k]^{-1/2}[C^{[k]}(\hat{r}_1)\times(l_1,\hat{r}_1|w^{[0k_1]}|l_1',\hat{r}_1')]_{00}^{[01]}\int d\hat{r}_2[C^{[k]}(\hat{r}_2)\times(l_2,\hat{r}_2|w^{[0k]}|l_2',\hat{r}_2)]^{[00]} \\ &= \delta_{\kappa 0}\delta_{k_2k}(2[k_1]/[k])^{1/2}\sum_{\bar{l}}(-1)^{l_1+l_1'+k_1+k}(\bar{l}\|C^{[k]}\|l_1)(l_2'\|C^{[k]}\|l_2)\begin{Bmatrix}k_1 & 1 & k_2\\ \bar{l} & l_1 & l_1'\end{Bmatrix}(\bar{l},\hat{r}_1|w_{00}^{[01]}|l_1',\hat{r}_1'). \end{aligned} \tag{4.10a}$$

A similar procedure leads to

$$J_k' = \delta_{\kappa 0}\delta_{k_2k}\left(\frac{2[k_1]}{[k]}\right)^{1/2}\sum_{\bar{l}}(-1)^k(l_1'\|C^{[k]}\|\bar{l})(l_2'\|C^{[k]}\|l_2)\begin{Bmatrix}k_1 & 1 & k_2\\ \bar{l} & l_1' & l_1\end{Bmatrix}(l_1,\hat{r}_1|w_{00}^{[01]}|\bar{l},\hat{r}_1'). \tag{4.10b}$$

The permutation of coordinates $\hat{r}_1'$ and $\hat{r}_2'$ in the tensor products $[\ldots]^{[\kappa k]}$ of Eqs. (4.8a) and (4.8b) leads to two other spin-angular integrals,

$$K_k(l_1l_2,\,l_1'l_2';\,\kappa k_1k_2) = \int d\hat{r}_2\, d\hat{r}_2'\,\delta(\hat{r}_2-\hat{r}_2')P_k(\hat{r}_1\cdot\hat{r}_2)[(l_1,\hat{r}_1|w^{[\kappa k_1]}|l_1',\hat{r}_2')\times(l_2,\hat{r}_2|w^{[\kappa k_2]}|l_2',\hat{r}_1')]_{00}^{[01]}, \tag{4.11a}$$

$$K'_k(l_1 l_2, l'_1 l'_2; \kappa k_1 k_2) = \int d\hat{r}_2\, d\hat{r}'_2\, \delta(\hat{r}_2 - \hat{r}'_2)[(l_1, \hat{r}_1|w^{[\kappa k_1]}|l'_1, \hat{r}'_2)\times(l_2, \hat{r}_2|w^{[\kappa k_2]}|l'_2, \hat{r}'_1)]^{[01]}_{00} P_k(\hat{r}'_1\cdot\hat{r}'_2). \tag{4.11b}$$

The integral K_k is calculated by first applying to the two w matrices a recoupling procedure which interchanges $(l'_1\hat{r}'_2)$ and $(l'_2\hat{r}'_1)$. Thus, K_k becomes a linear combination of a set of spin-angular integrals J_k, i.e.,

$$K_k = \sum_{j_1 j_2 \bar{\kappa}} (-1)^{\kappa+\bar{\kappa}}[\kappa,\bar{\kappa}] \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & \kappa \\ \frac{1}{2} & \frac{1}{2} & \kappa \\ \bar{\kappa} & \bar{\kappa} & 0 \end{Bmatrix} (-1)^{l'_1+l'_2+k_2+j_2}[k_1 k_2 j_1 j_2]^{1/2} \begin{Bmatrix} l_1 & l'_2 & k_1 \\ l'_2 & l_2 & k_2 \\ j_1 & j_2 & 1 \end{Bmatrix} J_k(l_1 l_2, l'_2 l'_1, \bar{\kappa} j_1 j_2)$$

$$= (-1)^{\kappa}\left(\frac{[\kappa]}{2}\right)^{1/2}\sum_{\bar{l}} (-1)^{1+l'_1+l'_2+k_1}[k_1 k_2]^{1/2}(\bar{l}\|C^{[k]}\|l_1)(l'_1\|C^{[k]}\|l_2)\begin{Bmatrix} k_2 & 1 & k_1 \\ \bar{l} & l_2 & l'_2 \end{Bmatrix}\begin{Bmatrix} \bar{l} & l_2 & k_1 \\ l'_1 & l_1 & k \end{Bmatrix}(\bar{l}, \hat{r}_1|w^{[01]}_{00}|l'_2, \hat{r}'_1). \tag{4.12a}$$

A similar calculation leads to

$$K'_k = (-1)^{\kappa}\left(\frac{[\kappa]}{2}\right)^{1/2}\sum_{\bar{l}} (-1)^{k+\bar{l}+l'_1+k_2}[k_1 k_2]^{1/2}(l'_1\|C^{[k]}\|l_2)(l'_2\|C^{[k]}\|\bar{l})\begin{Bmatrix} k_1 & 1 & k_2 \\ \bar{l} & l'_1 & l_1 \end{Bmatrix}\begin{Bmatrix} \bar{l} & l'_1 & k_2 \\ l_2 & l'_2 & k \end{Bmatrix}(l_1, \hat{r}_1|w^{[01]}_{00}|\bar{l}, \hat{r}'_1). \tag{4.12b}$$

Other spin-angular integrals resulting from the coordinate permutations P_{12} and $P_{12}P_{1'2'}$ follow immediately by interchanging two w matrices in J_k, J'_k, K_k, and K'_k. Thus, we obtain a general formula

$$\begin{aligned}
&\int d\vec{r}_2\, d\vec{r}'_2\, \delta(\vec{r}_2 - \vec{r}'_2)(|\vec{r}_1 - \vec{r}_2|^{-1} - |\vec{r}'_1 - \vec{r}'_2|^{-1})\{(1 - P_{12})(1 - P_{1'2'})\chi_{l_1}(r_1)\chi_{l_2}(r_2) \\
&\qquad\times[(l_1, \hat{r}_1|w^{[\kappa k_1]}|l'_1, \hat{r}'_1)\times(l_2, \hat{r}_2|w^{[\kappa k_2]}|l'_2, \hat{r}'_2)]^{[01]}_{00}\chi_{l'_1}(\hat{r}'_1)\chi_{l'_2}(\hat{r}'_2)\} \\
&= (-1)^{k_1}(1 - P_{l_1 l_2}P_{l'_1 l'_2}P_{k_1 k_2})\sum_{k,\bar{l}}(\bar{l}, \hat{r}_1|w^{[01]}_{00}|l'_1, \hat{r}'_1)(-1)^{l_1+l'_1+k}\left(\frac{2[k_1]}{[k_2]}\right)^{1/2}\begin{Bmatrix} k_1 & 1 & k_2 \\ \bar{l} & l_1 & l'_1 \end{Bmatrix} \\
&\times\left[\delta_{\kappa 0}\delta_{k_2 k}(\bar{l}\|V^k(\chi_{l'_2}, \chi_{l_2}; r_1)\|l_1)\chi_{l_1}(r_1) - (-1)^{\kappa}\left(\frac{[\kappa]}{2}\right)^{1/2}[k_2]\begin{Bmatrix} \bar{l} & l_1 & k_2 \\ l'_2 & l_2 & k \end{Bmatrix}(\bar{l}\|V^k(\chi_{l'_2}, \chi_{l_1}; r_1)\|l_2)\chi_{l_2}(r_1)\right]\chi_{l'_1}(r'_1) \\
&- (-1)^{k_2}(1 - P_{l_1 l_2}P_{l'_1 l'_2}P_{k_1 k_2})\sum_{k,\bar{l}}(l_1, \hat{r}_1|w^{[01]}_{00}|\bar{l}, \hat{r}'_1)(-1)^{\bar{l}+l'_1+k}\left(\frac{2[k_1]}{[k_2]}\right)^{1/2}\begin{Bmatrix} k_1 & 1 & k_2 \\ \bar{l} & l'_1 & l_1 \end{Bmatrix}\chi_{l_1}(r_1) \\
&\times\left[\delta_{\kappa 0}\delta_{k_2 k}\chi_{l'_1}(r'_1)(l'_1\|V^k(\chi_{l'_2}, \chi_{l_2}; r'_1)\|\bar{l}) - (-1)^{\kappa}\left(\frac{[\kappa]}{2}\right)^{1/2}[k_2]\begin{Bmatrix} \bar{l} & l'_1 & k_2 \\ l_2 & l'_2 & k \end{Bmatrix}\chi_{l'_2}(r'_1)(l'_2\|V^k(\chi_{l'_1}, \chi_{l_2}; r'_1)\|\bar{l})\right],
\end{aligned} \tag{4.13}$$

where the operator $P_{l_1 l_2}$ interchanges the quantum numbers l_1 and l_2. Each radial integral over the electron-electron interaction is represented as a 2^k-pole potential function; from the point of view of space rotations, this potential constitutes a reduced matrix element and is defined as

$$(l\|V^k(a, b; r)\|l') = (l\|C^{[k]}\|l')(l_a\|C^{[k]}\|l_b)\int_0^{\infty} dr'\, a(r')b(r')\frac{r^k_<}{r^{k+1}_>}, \tag{4.14}$$

where $a(r')$ and $b(r')$ indicate two radial wave functions. The two terms $1 + P_{12}P_{1'2'}$ on the left-hand side of Eq. (4.13) yield the first terms inside each of the two large square brackets on the right-hand side of Eq. (4.13), while the other two terms, $-P_{12}$ and $-P_{1'2'}$, yield the second term in each bracket.

Having derived the general formula Eq. (4.13), we proceed to calculate the term (4.6). The first term of $(\vec{r}_1, \vec{r}_2|\Gamma|\vec{r}'_1, \vec{r}'_2)$ then leads to

$$(l_e,\hat{r}_1|w_{00}^{[01]}|l_g,\hat{r}_1')[V_{l_e}^N(r_1)\psi_e(r_1)\chi_g(r_1')-\psi_e(r_1)\chi_g(r_1')V_{l_g}^N(r_1')]-(l_g,\hat{r}_1|w_{00}^{[01]}|l_e,\hat{r}_1')[\chi_g(r_1)\phi(r_1')V_{l_e}^N(r_1')-V_{l_g}^N(r_1)\chi_g(r_1)\phi(r_1')]$$
$$-\sum_{\bar{l}}\sum_{s}^{\text{occup}}(\bar{l},r_1|w_{00}^{[01]}|l_s,r_1')\Bigg[\tfrac{2}{3}[(\bar{l}\|V^1(\chi_g,\psi_e;r_1)\|l_s)+(\bar{l}\|V^1(\phi,\chi_g;r_1)\|l_s)]\chi_s(r_1)$$
$$+\sum_k(-1)^k\left(\begin{Bmatrix}\bar{l}&k&l_e\\l_g&1&l_s\end{Bmatrix}(\bar{l}\|V^k(\chi_g,\chi_s;r_1)\|l_e)\psi_e(r_1)+\begin{Bmatrix}\bar{l}&k&l_g\\l_e&1&l_s\end{Bmatrix}(\bar{l}\|V^k(\phi,\chi_s;r_1)\|l_g)\chi_g(r_1)\right)\Bigg]\chi_s(r_1')$$
$$+\sum_{\bar{l}}\sum_{s}^{\text{occup}}(l_s,r_1|w_{00}^{[01]}|\bar{l},r_1')\chi_s(r_1)\Bigg[\tfrac{2}{3}\chi_s(r_1')[(l_s\|V^1(\chi_g,\psi_e;r_1')\|\bar{l})+(l_s\|V^1(\phi,\chi_g;r_1')\|\bar{l})]$$
$$+\sum_k(-1)^k\left(\begin{Bmatrix}\bar{l}&k&l_g\\l_e&1&l_s\end{Bmatrix}\chi_g(r_1')(l_g\|V^k(\chi_s,\psi_e;r_1')\|\bar{l})\right.$$
$$\left.+\begin{Bmatrix}\bar{l}&k&l_e\\l_g&1&l_s\end{Bmatrix}\phi(r_1')(l_e\|V^k(\chi_s,\chi_g;r_1')\|\bar{l})\right)\Bigg]\,, \tag{4.15}$$

where

$$V_l^N(r)f_l(r)=\sum_s^{\text{occup}}\left(\frac{[l_s]}{[l]}\right)^{1/2}2(l\|V^0(\chi_s,\chi_s;r)\|l)f_l(r)-\frac{1}{[l]}\sum_s^{\text{occup}}\sum_k(-1)^k(l\|V^k(\chi_s,f_l;r)\|l_s)\chi_s(r)\,. \tag{4.16}$$

To calculate the contributions from the second and third terms of $(\vec{r}_1,\vec{r}_2|\Gamma|\vec{r}_1',\vec{r}_2')$, we need only consider the first term in each of the large square brackets on the right-hand side of Eq. (4.13). Thus, from the second term of $(\vec{r}_1,\vec{r}_2|\Gamma|\vec{r}_1',\vec{r}_2')$, we obtain

$$(l_e,\hat{r}_1|w_{00}^{[01]}|l_g,\hat{r}_1')\sum_k\frac{1}{[l_e]}\frac{A_k}{A_1}(l_e\|V^k(\phi,\chi_g;r_1)\|l_g)\chi_g(r_1)\chi_g(r_1')$$
$$-\sum_{k,\bar{l}}(l_g,\hat{r}_1|w_{00}^{[01]}|\bar{l},\hat{r}_1')\chi_g(r_1)\left(\frac{A_k}{A_1}\begin{Bmatrix}\bar{l}&l_g&k\\l_e&l_g&1\end{Bmatrix}\chi_g(r_1')(l_g\|V^k(\phi,\chi_g;r_1')\|\bar{l})-B_k(l_g,l_e,\bar{l})\phi(r_1')(l_e\|V^k(\chi_g,\chi_g;r_1')\|\bar{l})\right)$$
$$+\sum_{k,\bar{l}}(\bar{l},\hat{r}_1|w_{00}^{[01]}|l_e,\hat{r}_1')C_k(l_g,l_e,\bar{l})(\bar{l}\|V^k(\chi_g,\chi_g;r_1)\|l_g)\chi_g(r_1)\phi(r_1')\,, \tag{4.17}$$

where

$$A_k=(-1)^{1+k}\frac{2}{[k]^{1/2}}c_{0k}(l_e,l_g)=\sum_{S,L}\tfrac{1}{2}[1+(-1)^{S+L}]\begin{Bmatrix}l_e&l_e&L\\l_g&l_g&k\end{Bmatrix}(-1)^Lb_{SL}\,, \tag{4.18}$$

$$B_k(l,l',\bar{l})=\sum_{k_2}A_{k_2}[k_2]\begin{Bmatrix}1&k&k_2\\l&l'&l\end{Bmatrix}\begin{Bmatrix}l'&l&k_2\\1&k&\bar{l}\end{Bmatrix}=\sum_{S,L}\tfrac{1}{2}[1+(-1)^{S+L}](-1)^{\bar{l}+k}\begin{Bmatrix}l&k&l\\1&\bar{l}&l\\l'&l'&L\end{Bmatrix}b_{SL}\,, \tag{4.19}$$

$$C_k(l,l',\bar{l})=\sum_{k_2}(-1)^{k_2}A_{k_2}[k_2]\begin{Bmatrix}1&k&k_2\\l&l'&l\end{Bmatrix}\begin{Bmatrix}l&l'&k_2\\1&k&\bar{l}\end{Bmatrix}=\sum_{S,L}\tfrac{1}{2}[1+(-1)^{S+L}](-1)^{\bar{l}+k}\begin{Bmatrix}l&\bar{l}&L\\l'&l'&1\end{Bmatrix}\begin{Bmatrix}l&\bar{l}&L\\l&l&k\end{Bmatrix}b_{SL}\,, \tag{4.20}$$

with $(l,l')=(l_g,l_e)$ or (l_e,l_g). Similarly, the third term in Eq. (3.36) gives

$$-(l_e,\hat{r}_1|w_{00}^{[01]}|l_g,\hat{r}_1')\sum_k\frac{A_k}{[l_g]}\psi_e(r_1)[\varphi_a(r_1')(l_e\|V^k(\varphi_b,\chi_g;r_1')\|l_g)+\varphi_b(r_1')(l_e\|V^k(\varphi_a,\chi_g;r_1')\|l_g)]$$
$$+\sum_{k,\bar{l}}(\bar{l},\hat{r}_1|w_{00}^{[01]}|l_e,\hat{r}_1')\left(A_k\begin{Bmatrix}\bar{l}&l_e&k\\l_g&l_e&1\end{Bmatrix}[(\bar{l}\|V^k(\varphi_b,\chi_g;r_1)\|l_e)\psi_e(r_1)\varphi_a(r_1')+(\bar{l}\|V^k(\varphi_a,\chi_g;r_1)\|l_e)\psi_e(r_1)\varphi_b(r_1')]\right.$$
$$\left.-B_k(l_e,l_g,\bar{l})[(\bar{l}\|V^k(\varphi_a,\psi_e;r_1)\|l_g)\chi_g(r_1)\varphi_b(r_1')+(\bar{l}\|V^k(\varphi_b,\psi_e;r_1)\|l_g)\chi_g(r_1)\varphi_a(r_1')]\right)$$
$$-\sum_{k,\bar{l}}(l_g,\hat{r}_1|w_{00}^{[01]}|l_e,\hat{r}_1')\chi_g(r_1)C_k(l_e,l_g,\bar{l})[\varphi_a(r_1')(l_e\|V^k(\varphi_b,\psi_e;r_1')\|\bar{l})+\varphi_b(r_1')(l_e\|V^k(\varphi_a,\psi_e;r_1')\|\bar{l})]\,. \tag{4.21}$$

Substituting Eqs. (4.5), (4.15), (4.17), and (4.21) into Eq. (4.4) and setting $l_g=1$, $l_e=2$, $g=3p$, $s=nl$, and $\psi_e=\psi$, we obtain Eq. (17) of Ref. 1 with its explicit expression given in the Appendix A of Ref. 1.

V. GENERAL APPROACH

Consider a pair of atomic states $|a)$ and $|a')$ with antisymmetrized LS-coupled wave functions $(\vec{r}_1,\ldots\vec{r}_N|\alpha SLM_SM_L)$ and $(\vec{r}'_1,\ldots\vec{r}'_N|\alpha'S'L'M'_SM'_L)$, where α and α' represent any additional information on the configuration (or configuration admixture), coupling scheme, etc. To the transition from state $|a')$ to $|a)$ we associate double-tensor transition matrices defined by

$$\Psi_a\Psi^*_{a'}=(\vec{r}_1,\ldots\vec{r}_i,\ldots\vec{r}_N|\,\Gamma^{[\kappa k]}_{\pi q}\,|\vec{r}'_1,\ldots\vec{r}'_j,\ldots\vec{r}'_N)$$

$$=\sum_{M_SM_LM'_SM'_L}(\cdots\vec{r}_i\circ\cdots|\alpha SLM_SM_L)\,(\alpha'S'L'M'_SM'_L|\cdots\vec{r}'_j\cdots)(-1)^{S'-M'_S+L'-M'_L}$$
$$\times(SM_S,S'-M'_S|SS'\kappa\pi)(LM_L,L'-M'_L|LL'kq)\,. \tag{5.1}$$

The tensor indices (κ,k,π,q) range over the $(2S+1)(2L+1)(2S'+1)(2L'+1)$ combinations leading to nonzero Wigner coefficients in Eq. (5.1). In the example of Ar dipole transitions studied in Ref. 1, the sum in Eq. (5.1) reduces to a single term with unit coefficient because the $|a')$ state is identified as ^1S, with $S'=L'=0$, and the $|a)$ state as ^1P $(S=0,L=1)$, whereby $\kappa=0$, $k=L=1$, and $q=M_L$. [If the spin and orbital momenta were coupled in the two wave functions to yield total quantum numbers J and J', one would construct for each pair (J,J') single-tensor transition matrices $\Gamma^{[k]}_q$, using a single Wigner coefficient $(-1)^{J'-M'}\times(JM,J'-M'|JJ'kq).$]

The main task to be considered is the derivation from Eq. (5.1) of nth-order transition matrices, by $(N-n)$-fold integration. To this end one should isolate from each of the two N-electron wave functions a common parent state of $N-n$ electrons. We actually consider two distinct parent states $|\tilde{\alpha}\tilde{L}\tilde{S})$ and $|\tilde{\alpha}'\tilde{L}'\tilde{S}')$ to allow for the possibility—utilized in Ref. 1—that these two states differ in their radial parts, which must, however, be nonorthogonal; in any event, we must have $\tilde{S}'=\tilde{S}$ and $\tilde{L}'=\tilde{L}$. We consider, then, the parentage expansion of state $|a)$:

$$(\vec{r}_1,\ldots\vec{r}_i,\ldots\vec{r}_N|\alpha SLM_LM_S)=\Big(\sum_P(-1)^PP(1,\ldots n;n+1,\ldots N)\Big)$$
$$\times\sum_{\bar{\alpha}\bar{S}\bar{L}\bar{M}_S\bar{M}_L,\tilde{\alpha}\tilde{S}\tilde{L}\tilde{M}_S\tilde{M}_L}(\vec{r}_1,\ldots\vec{r}_n|\bar{\alpha}\bar{S}\bar{L}\bar{M}_S\bar{M}_L)(\vec{r}_{n+1},\ldots\vec{r}_N|\tilde{\alpha}\tilde{S}\tilde{L}\tilde{M}_S\tilde{M}_L)$$
$$\times(\bar{S}\bar{M}_S\tilde{S}\tilde{M}_S|\bar{S}\tilde{S}SM_S)(\bar{L}\bar{M}_L\tilde{L}\tilde{M}_L|\bar{L}\tilde{L}LM_L)(\bar{\alpha}\bar{S}\bar{L},\tilde{\alpha}\tilde{S}\tilde{L}|\alpha SL)\,. \tag{5.2}$$

On the right-hand side of this equation, the first factor ensures antisymmetrization with respect to the $\binom{N}{n}$ permutations P of one of the n electrons in the first group with one electron of the second group; when the Nth-order matrix is entered in Eq. (1.3), this factor will be dropped, together with the corresponding factor in the expansion of $|a')$, being replaced by the factor $\binom{N}{n}$ which appears in that equation. The second and third factors on the right-hand side of Eq. (5.2) are antisymmetrized wave functions of the n-electron state $|\bar{\alpha}\bar{S}\bar{L})$ and of its parent state $|\tilde{\alpha}\tilde{S}\tilde{L})$. The fourth and fifth factors are Wigner coefficients, and the last factor includes fractional parentage and/or any other coefficient relevant to the expansion.

The parentage expansion of $|a)$, Eq. (5.2), and the corresponding expansion of $|a')$, are substituted in Eq. (5.1), and the integral of Eq. (1.3) is evaluated. The orthonormality of spin-angular functions then restricts nonvanishing contributions to those of expansion terms which have $\tilde{M}_S=\tilde{M}'_S$ and $\tilde{M}_L=\tilde{M}'_L$, besides $\tilde{S}=\tilde{S}'$ and $\tilde{L}=\tilde{L}'$ and identical coupling within $\tilde{\alpha}$ and $\tilde{\alpha}'$. Each of the nonvanishing terms would reduce to unity if the radial parts were also orthonormal; we indicate the radial integral by $(\tilde{\alpha}'|\tilde{\alpha})$. The sums over magnetic quantum numbers, thus restricted, can be carried out analytically in terms of recoupling coefficients, observing, e.g., that a factor $(-1)^{\tilde{L}'-\tilde{M}'_L}\delta_{\tilde{M}'_L\tilde{M}_L}\delta_{\tilde{L}\tilde{L}'}$ can be expressed in terms of a Wigner coefficient by $(\tilde{L}\tilde{M}_L\tilde{L}'-\tilde{M}_{L'}|\tilde{L}\tilde{L}'00)[\tilde{L}]^{1/2}$. Consider that the orbital part of $\Gamma^{(\kappa k)}$, whose coupling was initially represented by $[(\bar{L}\tilde{L})L(\bar{L}'\tilde{L}')L']k$, becomes now $[(\bar{L}\bar{L}')k(\tilde{L}\tilde{L}')0]k$; the relevant transformation coefficient is

$$((\bar{L}\bar{L}')k(\tilde{L}\tilde{L}')0;k|(\bar{L}\tilde{L})L(\bar{L}'\tilde{L}')L';k) = (-1)^{k+L'+\bar{L}+\tilde{L}}[L,L']^{1/2}[\tilde{L}]^{-1/2}\begin{Bmatrix} L & L' & k \\ \bar{L}' & \bar{L} & \tilde{L} \end{Bmatrix}\delta_{\tilde{L}\tilde{L}'}.$$

The nth-order matrix is thus obtained as an expansion,

$$(\vec{r}_1,\ldots\vec{r}_n|\,\Gamma^{[\kappa k]}_{\pi q}|\,\vec{r}'_1,\ldots\vec{r}'_n) = \binom{N}{n}\sum_{\bar{\alpha}\bar{L}\bar{S}\bar{\alpha}'\bar{L}'\bar{S}'}(\vec{r}_1,\ldots\vec{r}_n|\,\Gamma^{[\kappa k]}_{\pi q}(\bar{\alpha}\bar{L}\bar{S},\bar{\alpha}'\bar{L}'\bar{S}')|\vec{r}'_1,\ldots\vec{r}'_n)$$
$$\times\sum_{\tilde{\alpha}\tilde{\alpha}'\tilde{S}\tilde{L}}(\tilde{\alpha}'|\tilde{\alpha})(-1)^{\kappa+S'+\bar{S}+\tilde{S}+k+L'+\bar{L}+\tilde{L}}\frac{[S,S',L,L']^{1/2}}{[\tilde{S},\tilde{L}]^{1/2}}\begin{Bmatrix} S & S' & \kappa \\ \bar{S}' & \bar{S} & \tilde{S} \end{Bmatrix}\begin{Bmatrix} L & L' & k \\ \bar{L}' & \bar{L} & \tilde{L} \end{Bmatrix}$$
$$\times(\bar{\alpha}\bar{S}\bar{L}\tilde{\alpha}\tilde{S}\tilde{L}|\alpha SL)(\alpha'S'L'|\bar{\alpha}'\bar{S}'\bar{L}'\tilde{\alpha}'\tilde{S}\tilde{L}), \qquad (5.3)$$

where the transition matrix on the right is the same as one would construct for a transition from the n-electron state $(\bar{\alpha}'\bar{S}'\bar{L}'\bar{M}'_S\bar{M}'_L|\vec{r}'_1,\ldots\vec{r}'_n)$ to $(\bar{\alpha}\bar{S}\bar{L}\bar{M}_S\bar{M}_L|\vec{r}_1,\ldots\vec{r}_n)$. In the comparatively simple example of Ref. 1, the multiple sum of Eq. (5.3) reduces to the three groups of terms of Eq. (3.36).

First-order matrices obtained by this procedure have their spin-angular dependence represented as a linear combination of matrices $(l,\hat{r}_1|w^{[\kappa k]}_{\pi q}|\,l',\hat{r}'_1)$ with various indices (l,l'). For second- or higher-order matrices, the representation of angular dependence given by Eq. (5.3) differs from that of Eq. (3.36), but they may be transformed into one another by recoupling. In Eq. (5.3), the spin-angular variables of $(\vec{r}_1,\ldots\vec{r}_n)$—or $(\vec{r}'_1,\ldots\vec{r}'_n)$—are understood to be coupled into a wave function with quantum numbers $(\bar{\alpha}\bar{S}\bar{L})$—or $(\bar{\alpha}'\bar{S}'\bar{L}')$—the final double tensor being then constructed from these two functions. In Sec. III and in Ref. 1, on the contrary, the spin-angular factors of each pair of electron variables $(\hat{r}_i,\hat{r}'_j)$ are initially coupled to form a double tensor $(l,\vec{r}_i|w^{[\kappa k]}|\,l',\vec{r}'_j)$, after which two or more such factors for different pairs of variables and with different (κ,k) are multiplied tensorially and combined to yield the complete matrix $\Gamma^{[\kappa k]}$. Further experience will be required to assess whether or when either of these alternative representations is preferable.

That the expansion into single-electron $w^{[\kappa k]}$ matrices need not be preferable is suggested by the following circumstance. The developments of Secs. III and IV have utilized successive recoupling transformations, first from the coefficients b_{SL} to $c_{\kappa k}$, in Eq. (3.18), additional ones in the construction of the second-order matrix, Eq. (3.36), and again in the multiplication by the angular factor of the Hamiltonian, $P_k(\hat{r}_1\cdot\hat{r}_2)$, in Sec. IV. Eventually, however, various summations could be performed analytically—essentially, by multiplication of transformation matrices—condensing multiple products of $6j$ coefficients into simpler forms, each of which corresponds to a single recoupling operation. It then seems possible that the whole treatment of spin-angular factors might be funneled into a single recoupling transformation, as has been done previously[7] for the construction of interaction matrix elements for ordinary calculations of spectroscopy.

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†Present address: Physics Department, University of Southern California, Los Angeles, Calif. 90007.

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