

## Single-particle potential for photoexcited electron orbitals of open-shell atoms

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A single-particle potential for the calculation of photoexcited electron orbitals is introduced. This potential is defined to include exactly all of the first-order electron correlations that appear in the diagrammatic perturbation series of the dipole polarizability and that contain potential corrections in the intermediate state. The angular coefficients that are associated with this potential can be written in the form of an average term plus a correction to the average. It is demonstrated that the correction to the average contribution is dependent only upon the initial-state coupling of the atom. Additionally, a trivial relationship exists between the correction to the average contributions for conjugate initial-state configurations. The angular coefficients are tabulated for all of the  $s^n$ ,  $p^n$ , and  $d^n$  initial-state  $LS$  couplings that are possible. Supplementary analytic relationships are also presented.

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### I. INTRODUCTION

The interaction between an open-shell atom and an external time-dependent electric field is analyzed in this paper. Specifically, an investigation is made in order to define a general single-particle potential for photoexcited electron orbitals.

A previous investigation into this problem was made by Qian, Carter, and Kelly [1] (QCK). The analysis in the QCK paper was performed within the framework of many-body perturbation theory and examined the first-order corrections that appeared in the perturbation series of an exact dipole matrix element. This paper will differ from the QCK paper in two respects and arrive at slightly different results: the definition of the potential in this paper will be established using the first-order diagrammatic perturbation series of the dipole polarizability; additionally, the analytic expressions of the angular coefficients that are associated with this potential will be presented.

The dipole polarizability of an atom is an important parameter describing the interaction between the atom and an external field. For example, if we have the following external electric field:

$$\mathbf{E} = \left[ \frac{E_0}{2} e^{-i\omega t} + \frac{E_0^*}{2} e^{i\omega^* t} \right] \hat{\mathbf{z}}, \quad (1)$$

and if we use the variable  $\mathbf{P}$  to represent the induced electric dipole moment of the atom, then the diagonal component of the frequency-dependent dipole polarizability  $\alpha(\omega)$  is a measure of the linear response of the atom to the external field in the following manner:

$$\mathbf{P} = \left[ \alpha(\omega) \frac{E_0}{2} e^{-i\omega t} + \alpha^*(\omega) \frac{E_0^*}{2} e^{i\omega^* t} \right] \hat{\mathbf{z}}. \quad (2)$$

The physical processes that can be investigated with accurate calculations of  $\alpha(\omega)$  include the ac Stark shift [2],

photoionization [3], and the London dispersion forces between two atoms [4].

In the previous calculations where the QCK potential for open-shell atoms has been used, the appropriate angular coefficients of the potential that is introduced in this paper and the QCK potential are very close, quantitatively. This property can be attributed to the similarity of the initial step in both definitions. Despite this similarity, the analytic properties of the potential that is introduced in this paper are not shared, and do not have counterparts with the QCK potential. One of the most significant properties is that the angular coefficients can be written in the form of an average term plus a correction to the average. It will be shown that the correction to the average contribution is dependent only upon the initial-state coupling. Additionally, it will be demonstrated that a trivial relationship exists between the correction to the average contributions for conjugate initial-state configurations.

Section II of this paper reviews the algorithm for the construction of this potential, Sec. III presents some of the analytic properties that are associated with this definition, and the conclusions are presented in Sec. IV. Additionally, a class of the angular coefficients that are associated with this potential is tabulated for all of the  $s^n$ ,  $p^n$ , and  $d^n$  initial-state  $LS$  couplings that are possible.

### II. ALGORITHM FOR THE POTENTIAL

The Hamiltonian for an atom of nuclear charge  $Z$  consisting of  $N$  electrons in an external field has the form

$$H = H_0 + H_c + V_{\text{ext}}, \quad (3a)$$

with

$$H_0 = \sum_{i=1}^N \left[ -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + V_i \right] = \sum_{i=1}^N h_i, \quad (3b)$$

$$H_c = \sum_{\substack{i,j=1 \\ i < j}}^N \frac{1}{r_{ij}} - \sum_{i=1}^N V_i, \quad (3c)$$

and

$$V_{\text{ext}} = \left[ \frac{E_0}{2} e^{-i\omega t} + \frac{E_0^*}{2} e^{i\omega^* t} \right] \sum_{i=1}^N z_i. \quad (3d)$$

Throughout this paper, atomic units will be used except where it is noted to be otherwise. The analysis will follow the formalism of the many-body perturbation theory (MBPT) of Brueckner [5] and Goldstone [6] as it has been applied to atoms [7,8]. Additionally, the results will be presented within the context of  $LS$  coupling.

The expression in Eq. (3d) represents the perturbing influence of the external electric field of Eq. (1). The interaction Hamiltonian  $V_{\text{ext}}$  that is shown in Eq. (3d) is in the length gauge.

The variable  $V_i$  in Eqs. (3b) and (3c) is a single-particle Hermitian potential that will approximate the Coulomb repulsion between the electrons in the atom and that will render the zeroth-order Hamiltonian  $H_0$  solvable:

$$h_i |\phi_i\rangle = \varepsilon_i |\phi_i\rangle. \quad (4)$$

A general form of the potential  $V_i$  that will be under consideration is [9]

$$V_i = V_i^{(\text{HF})} + \left[ 1 - \sum_{j=1}^N |\phi_j\rangle \langle \phi_j| \right] (V_i^{(N-1)} - V_i^{(\text{HF})}) \times \left[ 1 - \sum_{j=1}^N |\phi_j\rangle \langle \phi_j| \right]. \quad (5)$$

This potential is Hermitian. The operator  $V_i^{(\text{HF})}$  is the restricted Hartree-Fock potential for the  $N$  orbitals that are occupied in the initial state of the atom  $\{ \phi_i | i \in (1, \dots, N) \}$ . The operator  $V_i^{(N-1)}$  is an arbitrary frozen-core Hermitian potential for the orbitals that are not occupied in the initial state of the atom  $\{ \phi_i | i \notin (1, \dots, N) \}$ .

The  $N$  electron orbitals that are occupied in the initial state of the atom are referred to as *core* orbitals and are indicated by the use of the subindices  $a$  and  $b$ , or

$$\{ \phi_a \} = \{ \phi_b \} = \{ \phi_i | i \in (1, \dots, N) \}. \quad (6a)$$

The remaining solutions of Eq. (4) that are not occupied in the initial state of the atom are referred to as *excited* orbitals and are indicated by the use of the subindex  $r$ , or

$$\{ \phi_r \} = \{ \phi_i | i \notin (1, \dots, N) \}. \quad (6b)$$

The use of the subindex  $i$  will indicate a summation over both the core and excited orbitals

$$\{ \phi_i \} = \{ \phi_r \} \cup \{ \phi_a \} = \{ \phi_r \} \cup \{ \phi_b \}. \quad (6c)$$

The use of the  $a$ ,  $b$ ,  $r$ , and  $i$  subindices follows that of Lindgren and Morrison [8]. Using this notation, Eq. (5) can be rewritten as

$$V_i = V_i^{(\text{HF})} + \left[ 1 - \sum_a |\phi_a\rangle \langle \phi_a| \right] (V_i^{(N-1)} - V_i^{(\text{HF})}) \times \left[ 1 - \sum_a |\phi_a\rangle \langle \phi_a| \right]. \quad (7a)$$

The potential  $V_i$  defined in Eq. (7a) will have the following properties with respect to the *core*  $|\phi_a\rangle$  and *excited*  $|\phi_r\rangle$  orbitals:

$$\langle \phi_a | V_i | \phi_a \rangle = \langle \phi_a | V_i^{(\text{HF})} | \phi_a \rangle, \quad (7b)$$

$$\langle \phi_a | V_i | \phi_r \rangle = \langle \phi_r | V_i | \phi_a \rangle = \langle \phi_a | V_i^{(\text{HF})} | \phi_r \rangle = \langle \phi_r | V_i^{(\text{HF})} | \phi_a \rangle, \quad (7c)$$

$$\langle \phi_r | V_i | \phi_r \rangle = \langle \phi_r | V_i^{(N-1)} | \phi_r \rangle, \quad (7d)$$

$$V_i | \phi_a \rangle = V_i^{(\text{HF})} | \phi_a \rangle, \quad (7e)$$

and

$$V_i | \phi_r \rangle = V_i^{(N-1)} | \phi_r \rangle - \sum_a |\phi_a\rangle \langle \phi_a | (V_i^{(N-1)} - V_i^{(\text{HF})}) | \phi_r \rangle. \quad (7f)$$

In order to obtain Eqs. (7b)–(7f), the condition  $\langle \phi_a | \phi_r \rangle = 0$  has been used. This orthogonality condition is an automatic result of the fact that  $V_i$  is a Hermitian potential, provided that  $\varepsilon_a \neq \varepsilon_r$ .

Notice that the definition of the potential  $V_i$  given in Eq. (7a) allows one freedom in the choice of the  $V_i^{(N-1)}$  potential for the excited orbitals. There are an infinite

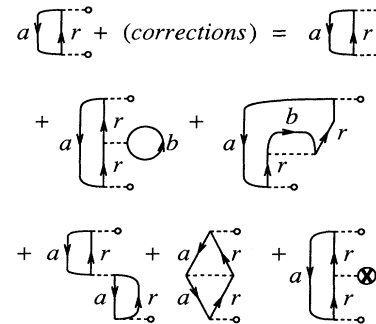


FIG. 1. The lowest-order Brueckner-Goldstone diagrams that contribute to the dipole polarizability and that contain diagonal corrections on the particle line. The expansion used here was developed by Kelly [12]. The time ordering of these diagrams proceeds from the bottom to the top. The solid lines with arrows refer to the orbitals in the basis set, and the direction of the arrow signifies the occupation status of the respective orbital. In the initial state of the system, all of the core orbitals are occupied and none of the excited orbitals is. An arrow pointing down indicates an unoccupied core orbital and an arrow pointing up indicates an occupied excited orbital. A dashed line connected to a small circle indicates a dipole interaction. A dashed line that connects two sets of arrows indicates a Coulomb interaction. The dashed line that is connected to the symbol  $\otimes$  indicates an interaction with the potential  $-V_i$ . To define the potential, we require that the first-order terms, which contribute to the (*corrections*), cancel.

number of potentials  $V_i$ , therefore, that can be defined over all of the orbitals  $|\phi_i\rangle$  and that behave as a restricted Hartree-Fock potential  $V_i^{(\text{HF})}$  when operating on the core orbitals  $|\phi_a\rangle$ , as indicated in Eqs. (7b) and (7e). The difference between the definitions of the potential  $V_i$  that are possible is the result of their operation on the noncore orbitals, as indicated in Eqs. (7d) and (7f). The purpose of this paper is to provide an explicit choice for the potential  $V_i^{(N-1)}$  such that certain classes of MBPT diagrams within the perturbation series of the dipole polarizability are automatically cancelled. The use of two potentials in a MBPT calculation, such as  $V_i^{(\text{HF})}$  and  $V_i^{(N-1)}$ , has been discussed by Ishihara and Poe [10]. They used the term "multiple basis set" in order to refer to the partitioning of the core and excited orbitals that occurs in Eqs. (7b)–(7f). Furthermore, Ishihara and Poe demonstrated, with a calculation of the photoionization cross section of helium, that the proper choice of a  $V_i^{(N-1)}$  potential could improve the convergence of a calculation [11]. In this pa-

per, the basic algorithm for the construction of the potential  $V_i^{(N-1)}$  will be derived through an analysis of the perturbation series of the dipole polarizability  $\alpha(\omega)$ . The diagrammatic series for  $\alpha(\omega)$  as developed by Kelly [12] will be used.

Some first-order corrections within the perturbation series of the dipole polarizability are shown in diagrammatic form in Fig. 1. These corrections are with respect to the correlation Hamiltonian  $H_c$  of Eq. (3c) and contain diagonal insertions on the particle line. The horizontal lines that end in open circles indicate dipole matrix elements. The horizontal lines that connect two sets of arrows indicate a Coulomb interaction  $r_{12}^{-1}$ , and the dashed line that connects to the symbol  $\otimes$  indicates an interaction with the potential  $-V_i$ . According to Eq. (7d), the specific matrix element will be with respect to the potential  $-V_i^{(N-1)}$ :  $\langle\phi_r| -V_i|\phi_r\rangle = \langle\phi_r| -V_i^{(N-1)}|\phi_r\rangle$ . Using wave functions composed of single determinants, Fig. 1 represents the following mathematical expression:

$$\begin{aligned}
& - \lim_{\eta \rightarrow 0^+} \sum_{a,r} \langle\phi_a|z|\phi_r\rangle \langle\phi_r|z|\phi_a\rangle \left[ \frac{1}{(\epsilon_a - \epsilon_r + \omega + i\eta)} + \frac{1}{(\epsilon_a - \epsilon_r - \omega - i\eta)} \right] + (\text{corrections}) \\
& = - \lim_{\eta \rightarrow 0^+} \sum_{a,r} \langle\phi_a|z|\phi_r\rangle \langle\phi_r|z|\phi_a\rangle \left[ \frac{1}{(\epsilon_a - \epsilon_r + \omega + i\eta)} + \frac{1}{(\epsilon_a - \epsilon_r - \omega - i\eta)} \right] \\
& - \lim_{\eta \rightarrow 0^+} \left[ \sum_{a,r,b} \langle\phi_a|z|\phi_r\rangle \langle\phi_r(1)\phi_b(2)|r_{12}^{-1}|\phi_r(1)\phi_b(2)\rangle \langle\phi_r|z|\phi_a\rangle \right. \\
& \quad - \sum_{a,r,b} \langle\phi_a|z|\phi_r\rangle \langle\phi_r(1)\phi_b(2)|r_{12}^{-1}|\phi_b(1)\phi_r(2)\rangle \langle\phi_r|z|\phi_a\rangle \\
& \quad + \sum_{a,r} \langle\phi_a|z|\phi_r\rangle \langle\phi_r(1)\phi_a(2)|r_{12}^{-1}|\phi_a(1)\phi_r(2)\rangle \langle\phi_r|z|\phi_a\rangle \\
& \quad - \sum_{a,r} \langle\phi_a|z|\phi_r\rangle \langle\phi_r(1)\phi_a(2)|r_{12}^{-1}|\phi_r(1)\phi_a(2)\rangle \langle\phi_r|z|\phi_a\rangle \\
& \quad \left. - \sum_{a,r} \langle\phi_a|z|\phi_r\rangle \langle\phi_r|V_i^{(N-1)}|\phi_r\rangle \langle\phi_r|z|\phi_a\rangle \right] \\
& \quad \times \left[ \frac{1}{(\epsilon_a - \epsilon_r + \omega + i\eta)(\epsilon_a - \epsilon_r + \omega + i\eta)} + \frac{1}{(\epsilon_a - \epsilon_r - \omega - i\eta)(\epsilon_a - \epsilon_r - \omega - i\eta)} \right]. \tag{8a}
\end{aligned}$$

The definition of  $V_i^{(N-1)}$  can be established by requiring that the terms, which contribute to the (*corrections*) in Fig. 1 and Eq. (8a), sum to zero. With this condition, one obtains the algorithm

$$\begin{aligned}
\langle\phi_r|V_i^{(N-1)}|\phi_r\rangle & = \frac{1}{\sum_{\substack{a',r' \\ a' \in \{nl\}}} \langle\phi_{a'}|z|\phi_{r'}\rangle \langle\phi_{r'}|z|\phi_{a'}\rangle} \\
& \times \sum_{\substack{a,r,b \\ a \in \{nl\}}} \langle\phi_a|z|\phi_r\rangle [\langle\phi_r(1)\phi_b(2)|r_{12}^{-1}|\phi_r(1)\phi_b(2)\rangle - \langle\phi_r(1)\phi_b(2)|r_{12}^{-1}|\phi_b(1)\phi_r(2)\rangle \\
& \quad + \langle\phi_r(1)\phi_a(2)|r_{12}^{-1}|\phi_a(1)\phi_r(2)\rangle - \langle\phi_r(1)\phi_a(2)|r_{12}^{-1}|\phi_r(1)\phi_a(2)\rangle] \langle\phi_r|z|\phi_a\rangle. \tag{8b}
\end{aligned}$$

Notice that the summation over the index  $a$  has been restricted to a summation over the single-particle magnetic ( $m_l$ ) and spin ( $m_s$ ) quantum numbers of a given subshell of the atom (subshell  $nl$ ). This is due to the degeneracy of the single-particle energy eigenvalues  $\epsilon_a$  for the orbitals within the subshell  $nl$ . Notice, also, that the potential is a scalar operator and it should be independent of  $m_l$  and  $m_s$  values. This dependence can be factored out for the interactions

from a given subshell and is why the summation over the  $r'$  index can be moved to the denominator on the right-hand side of Eq. (8b).

Equation (8b) is in terms of wave functions composed of single determinants. In terms of the multideterminant  $LS$ -coupled initial state

$$|G(M_L)\rangle = |(nl)^q LS\gamma M_L M_S\rangle, \quad (9a)$$

and an  $LS$ -coupled final channel

$$|F(I)\rangle = |((nl)^{q-1} L_I S_I \gamma_I; \epsilon l_F) L_F S_F \gamma_F M_L M_S\rangle, \quad (9b)$$

Eq. (8b) can be rewritten

$$\langle V^{N-1}(nl)^q:LS\gamma;(nl,\epsilon l_F)\rangle = \frac{\sum_{F,I,J,M_L} \langle G(M_L)|C_0^1|F(I)\rangle \langle F(I)|r_{12}^{-1}|F(J)\rangle \langle F(J)|C_0^1|G(M_L)\rangle}{\sum_{F',I',M_L'} \langle G(M_L')|C_0^1|F'(I')\rangle \langle F'(I')|C_0^1|G(M_L')\rangle}, \quad (9c)$$

where  $C_0^1$  is the spherical tensor operator appropriate to the dipole interaction [8]. The radial dependence and, therefore, the gauge dependence of the matrix element of the external field has been factored out. Notice that the potential depends only on the initial-state coupling and on the interaction between  $(nl,\epsilon l_F)$ . There is no dependence on the couplings  $L_F, S_F, \gamma_F$ , or  $L_I, S_I, \gamma_I$  from Eq. (9b).

The algorithm that is shown in Eqs. (8b) and (9c) differs slightly from the algorithm that was introduced in the QCK paper. For notational sake, the QCK potential will be denoted by  ${}_Q\langle V^{N-1}\rangle$ . The algorithm for the construction of the potential  ${}_Q\langle V^{N-1}\rangle$  is [1]

$${}_Q\langle V^{N-1}(nl)^q:LS\gamma;(nl,\epsilon l_F)\rangle = \sum_{M_L} \frac{1}{2L+1} \frac{\sum_{F,I,J} \langle G(M_L)|C_0^1|F(I)\rangle \langle F(I)|r_{12}^{-1}|F(J)\rangle \langle F(J)|C_0^1|G(M_L)\rangle}{\sum_{F',I'} \langle G(M_L)|C_0^1|F'(I')\rangle \langle F'(I')|C_0^1|G(M_L)\rangle}. \quad (10)$$

In the analysis in the QCK paper, the perturbation expansion of the dipole matrix element was used and the terms in this expansion are  $M_L$  dependent. The treatment of the variable  $M_L$  in Eq. (10) was introduced in order to remove this dependence.

The  ${}_Q\langle V^{N-1}\rangle$  potential has been used to generate excited orbitals of open-shell atoms in the past. In particular, it has been used in photoionization calculations of chlorine [1], yttrium [13], sulfur [14], and tungsten [15]. It is found in practice that the potentials defined in Eqs. (9c) and (10) are approximately equal,  $\langle V^{N-1}\rangle \approx {}_Q\langle V^{N-1}\rangle$ , for the  $\hbar\omega + n(l) \rightarrow \epsilon(l+1)$  transitions. In the case of tungsten [15], the largest difference between the definitions  $\langle V^{N-1}\rangle$  and  ${}_Q\langle V^{N-1}\rangle$  for the  $\hbar\omega + 5d \rightarrow \epsilon f$  transitions is of the order

$$\max \left[ \frac{|\langle V^{N-1}5d^4:5D;(5d,\epsilon f)\rangle - {}_Q\langle V^{N-1}5d^4:5D;(5d,\epsilon f)\rangle|}{|{}_Q\langle V^{N-1}5d^4:5D;(5d,\epsilon f)\rangle|} \right] \approx 1\%. \quad (11)$$

The analytic properties of  $\langle V^{N-1}\rangle$  will be examined in this paper rather than the properties of  ${}_Q\langle V^{N-1}\rangle$ . One of the most significant analytic properties is that a unique average can be defined for  $\langle V^{N-1}\rangle$  that extends over all of the initial-state configurations and couplings. There does not exist a similar relationship for  ${}_Q\langle V^{N-1}\rangle$  as defined in Eq. (10). Exact analytic expressions for the angular coefficients that are associated with  $\langle V^{N-1}\rangle$  will be presented in Sec. III for atoms with multiple open subshells in the initial state. Supplementary analytic relationships will also be presented.

### III. ANALYTIC PROPERTIES OF THE POTENTIAL

A complete derivation of the analytic properties that are presented in the paper can be found in Boyle [16]. The derivations were made beginning from Eq. (9c) and using the graphical technique of angular momentum coupling. Useful references for this technique are Lindgren

and Morrison [8] and Yutsis, Levinson, and Vanagas [17].

The results of this section will be presented within the context of photoexcitation. The photoionization cross section  $\sigma(\omega)$  is related to the frequency-dependent dipole polarizability in the following manner [3]:

$$\sigma(\omega) = \frac{4\pi\omega}{c} \text{Im}[\alpha(\omega)], \quad (12)$$

where  $c$  is the speed of light. Although the discussion of the physics in this section is from the standpoint of photoexcitation, the potential  $V_i^{(N-1)}$  is defined from the standpoint of the polarizability, and will be useful for the calculation of any physical quantity that can be determined from an accurate calculation of the polarizability.

The following process is considered for an atom with a single subshell in its initial state:

$$\hbar\omega + |(n_a l_a)^{q_a} : L_a S_a \gamma_a \rangle \rightarrow |(n_a l_a)^{q_a - 1} : L_I S_I \gamma_I \rangle + |\epsilon_r^{(a)} l_r^{(a)} \rangle. \quad (13)$$

In Eq. (13), the initial state of the atom is represented by  $|(n_a l_a)^{q_a} : L_a S_a \gamma_a \rangle$ . The variable  $\gamma_a$  represents any additional quantum number that might be necessary to completely specify the initial state, for example, a Racah seniority number. A possible ionic core left behind by the exiting electron is represented by  $|(n_a l_a)^{q_a - 1} : L_I S_I \gamma_I \rangle$ . The index  $I$  is used to indicate that

there may be many parent  $LS$  couplings that are possible. The electron that is photoexcited from the initial state is represented by  $|\epsilon_r^{(a)} l_r^{(a)} \rangle$ . The superscript  $a$  is used to indicate that the excited electron originated from subshell  $(a)$ , which was indicated by the subscripts on  $|(n_a l_a)^{q_a} : L_a S_a \gamma_a \rangle$ .

The  $\langle V^{N-1} \rangle$  potential for the excited orbital  $|\epsilon_r^{(a)} l_r^{(a)} \rangle$  is defined such that the (*corrections*) in Fig. 1 sum to zero. For the potential interactions between the excited electron  $|\epsilon_r^{(a)} l_r^{(a)} \rangle$  and the subshell from which it originated  $|(n_a l_a)^{q_a} : L_a S_a \gamma_a \rangle$ , the algorithm of Eq. (9c) yields [16]

$$\begin{aligned} & \langle V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a ; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle \\ &= \sum_{\substack{L_{PP}, S_{PP}, \gamma_{PP}, \\ L_I, S_I, \gamma_I, \\ L_J, S_J, \gamma_J, \\ \kappa}} (-1)^{1+\kappa+L_{PP}+L_I+L_J+L_a} (q_a - 1) [l_a, l_a, l_r^{(a)}] \sqrt{[L_J, L_I]} \\ & \times (l_a^{q_a} L_a S_a \gamma_a \{ |l_a^{q_a-1} L_I S_I \gamma_I, l_a \rangle (l_a^{q_a-1} L_I S_I \gamma_I \{ |l_a^{q_a-2} L_{PP} S_{PP} \gamma_{PP}, l_a \rangle \\ & \times (l_a^{q_a-2} L_{PP} S_{PP} \gamma_{PP}, l_a \} |l_a^{q_a-1} L_J S_J \gamma_J \rangle (l_a^{q_a-1} L_J S_J \gamma_J, l_a \} |l_a^{q_a} L_a S_a \gamma_a \rangle \\ & \times \begin{Bmatrix} \kappa & l_r^{(a)} & l_r^{(a)} \\ 1 & l_a & l_a \end{Bmatrix} \begin{Bmatrix} \kappa & l_a & l_a \\ L_a & L_I & L_J \end{Bmatrix} \begin{Bmatrix} \kappa & l_a & l_a \\ L_{PP} & L_I & L_J \end{Bmatrix} \\ & \times \begin{Bmatrix} F^\kappa(n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \delta(S_I, S_J) \begin{Bmatrix} \kappa & l_a & l_a \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} \kappa & l_r^{(a)} & l_r^{(a)} \\ 0 & 0 & 0 \end{Bmatrix} \\ & + \sum_{\Omega} (-1)^{1+S_I+S_J} G^\Omega(n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) [\kappa] \sqrt{[S_J, S_I]} \begin{Bmatrix} \Omega & l_a & l_r^{(a)} \\ 0 & 0 & 0 \end{Bmatrix}^2 \\ & \times \begin{Bmatrix} S_J & \frac{1}{2} & S_a \\ S_I & \frac{1}{2} & S_{PP} \end{Bmatrix} \begin{Bmatrix} l_a & l_a & \kappa \\ l_r^{(a)} & l_r^{(a)} & \Omega \end{Bmatrix} \end{Bmatrix}. \quad (14) \end{aligned}$$

The notation for the multiplicity of an angular momentum value  $j$  that is used in Eq. (14) is

$$[j] = (2j + 1), \quad (15a)$$

$$[j_1, j_2] = (2j_1 + 1)(2j_2 + 1), \quad (15b)$$

and so on. The  $q_a$  are the initial-state occupation numbers of the subshell  $n_a l_a$ . The variables  $(l_a^{q_a} L_a S_a \gamma_a \{ |l_a^{q_a-1} L_I S_I \gamma_I, l_a \rangle$  and  $(l_a^{q_a-1} L_I S_I \gamma_I \{ |l_a^{q_a-2} L_{PP} S_{PP} \gamma_{PP}, l_a \rangle$  are coefficients of fractional parentage. The variables  $L_{PP}, S_{PP}$ , and  $\gamma_{PP}$  are the total orbital angular momentum, the total spin angular momentum, and any additional quantum numbers that may be necessary to completely specify the grandparents of the initial state  $|(n_a l_a)^{q_a} : L_a S_a \gamma_a \rangle$ . Notice that independent summations are carried out over the parents of the initial state, as indicated by the separate summations over the  $L_I, S_I, \gamma_I$ , and  $L_J, S_J, \gamma_J$  indices. Additionally, the quantities  $F^\kappa$  and  $G^\kappa$  are the usual  $F$  and  $G$  radial Coulomb integrals:

$$F^\kappa(n_i l_i, n_j l_j) = \int dr_1 \int dr_2 P_{n_i l_i}(r_1) P_{n_j l_j}(r_2) \frac{r_1^\kappa}{r_2^{\kappa+1}} \times P_{n_i l_i}(r_1) P_{n_j l_j}(r_2). \quad (15c)$$

and

$$G^\kappa(n_i l_i, n_j l_j) = \int dr_1 \int dr_2 P_{n_i l_i}(r_1) P_{n_j l_j}(r_2) \frac{r_1^\kappa}{r_2^{\kappa+1}} \times P_{n_j l_j}(r_1) P_{n_i l_i}(r_2). \quad (15d)$$

In Eqs. (15c) and (15d), the quotient  $P_{n_i l_i}(r)/r$  is the radial portion of the orbital  $\phi_i$ , and the subscript  $< (>)$  on the variable  $r$  indicate the use of the lesser (greater) of  $r_1$  and  $r_2$ . Notice that Eq. (14) is for the diagonal matrix elements of the potential  $\langle V_i^{(N-1)} \rangle$ , and not the single-particle operator  $V_i^{(N-1)}$ . If we are considering the single-particle operator

$$V_r^{N-1} = \sum_{\kappa, a} [q_a c(r, a, \kappa) J_{n_a l_a}^\kappa + q_a d(r, a, \kappa) K_{n_a l_a}^\kappa], \quad (16a)$$

then we will use the following notation for the diagonal matrix elements with respect to the excited orbital  $|\epsilon_r^{(a)} l_r^{(a)} \rangle$ :

$$\langle \varepsilon_r^{(a)} l_r^{(a)} | V_r^{N-1} | \varepsilon_r^{(a)} l_r^{(a)} \rangle = \sum_{\kappa, a} [q_a c(r, a, \kappa) F^\kappa(n_a l_a, \varepsilon_r^{(a)} l_r^{(a)}) + q_a d(r, a, \kappa) G^\kappa(n_a l_a, \varepsilon_r^{(a)} l_r^{(a)})] \quad (16b)$$

$$= \sum_a \langle V^{N-1}(n_a l_a, \varepsilon_r^{(a)} l_r^{(a)}) \rangle, \quad (16c)$$

where we have used the following properties of the radial operators  $J_{n_a l_a}^\kappa$  and  $K_{n_a l_a}^\kappa$ :

$$\langle \varepsilon_r^{(a)} l_r^{(a)} | J_{n_a l_a}^\kappa | \varepsilon_r^{(a)} l_r^{(a)} \rangle = F^\kappa(n_a l_a, \varepsilon_r^{(a)} l_r^{(a)}), \quad (17a)$$

and

$$\langle \varepsilon_r^{(a)} l_r^{(a)} | K_{n_a l_a}^\kappa | \varepsilon_r^{(a)} l_r^{(a)} \rangle = G^\kappa(n_a l_a, \varepsilon_r^{(a)} l_r^{(a)}). \quad (17b)$$

In Eqs. (16a)–(16c), the coefficients  $c(i, j, \kappa)$  and  $d(i, j, \kappa)$  are the angular coefficients that are associated with the potential  $V_i$  operating on the orbital  $\phi_i$ . The use of the  $c(i, j, \kappa)$  and  $d(i, j, \kappa)$  coefficients follows that of Lindgren and Morrison [8].

Throughout this paper, the diagonal matrix elements of  $V_i^{(N-1)}$  are determined, and it is assumed that the excited orbital  $|\varepsilon_r^{(a)} l_r^{(a)}\rangle$  occupies an initially vacant subshell. This condition will be true for excitations into the continuum.

Next, the photoexcitation transitions for an atom that contains two open subshells in its initial state will be considered:

$$\hbar\omega + |(((n_a l_a)^{q_a} : L_a S_a \gamma_a)(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab} S_{ab}\rangle \rightarrow |(((n_a l_a)^{q_a-1} : L_P^{(a)} S_P^{(a)} \gamma_P^{(a)})(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab}^{(P)} S_{ab}^{(P)}\rangle + |\varepsilon_r^{(a)} l_r^{(a)}\rangle. \quad (18)$$

For the potential interactions between the excited electron and the subshell from which the electron originated [subshell ( $a$ )], one obtains [16]

$$\langle V^{N-1}(((n_a l_a)^{q_a} : L_a S_a \gamma_a)(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab} S_{ab}; (n_a l_a, \varepsilon_r^{(a)} l_r^{(a)}) \rangle = \langle V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a; (n_a l_a, \varepsilon_r^{(a)} l_r^{(a)}) \rangle. \quad (19a)$$

This demonstrates that Eq. (14) is a general result for the electrons that are interacting with the subshell from which they originated. Subshell ( $b$ ) acts as a bystander for the  $(n_a l_a, \varepsilon_r^{(a)} l_r^{(a)})$  interaction.

For the potential interactions between the excited electron and a subshell from which the excited electron did not originate [subshell ( $b$ )], one obtains [16]

$$\begin{aligned} & \langle V^{N-1}(((n_a l_a)^{q_a} : L_a S_a \gamma_a)(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab} S_{ab}; (n_b l_b, \varepsilon_r^{(a)} l_r^{(a)}) \rangle \\ &= \sum_{\substack{L_P^{(b)}, S_P^{(b)}, \gamma_P^{(b)}, \\ L_P^{(a)}, S_P^{(a)}, \gamma_P^{(a)}, \\ \kappa}} (q_b) (-1)^{1+L_P^{(a)}+L_P^{(b)}+L_{ab}} [L_a, L_b, l_a, l_b, l_r^{(a)}] \\ & \quad \times (l_a^{q_a} L_a S_a \gamma_a \{ |l_a^{q_a-1} L_P^{(a)} S_P^{(a)} \gamma_P^{(a)}, l_a \} (l_a^{q_a-1} L_P^{(a)} S_P^{(a)} \gamma_P^{(a)}, l_a) \{ |l_a^{q_a} L_a S_a \gamma_a \} \\ & \quad \times (l_b^{q_b} L_b S_b \gamma_b \{ |l_b^{q_b-1} L_P^{(b)} S_P^{(b)} \gamma_P^{(b)}, l_b \} (l_b^{q_b-1} L_P^{(b)} S_P^{(b)} \gamma_P^{(b)}, l_b) \{ |l_b^{q_b} L_b S_b \gamma_b \} \\ & \quad \times \begin{Bmatrix} \kappa & l_a & l_a \\ 1 & l_r^{(a)} & l_r^{(a)} \end{Bmatrix} \begin{Bmatrix} \kappa & l_a & l_a \\ L_P^{(a)} & L_a & L_a \end{Bmatrix} \begin{Bmatrix} \kappa & l_b & l_b \\ L_P^{(b)} & L_b & L_b \end{Bmatrix} \begin{Bmatrix} \kappa & L_a & L_a \\ L_{ab} & L_b & L_b \end{Bmatrix} \\ & \quad \times \begin{Bmatrix} F^\kappa(n_b l_b, \varepsilon_r^{(a)} l_r^{(a)}) \begin{Bmatrix} \kappa & l_b & l_b \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} \kappa & l_r^{(a)} & l_r^{(a)} \\ 0 & 0 & 0 \end{Bmatrix} \\ & \quad + \sum_{\Omega} (-1)^{\Omega-S_P^{(a)}-S_P^{(b)}+S_{ab}} G^\Omega(n_b l_b, \varepsilon_r^{(a)} l_r^{(a)}) [S_a, S_b, \kappa] \\ & \quad \times \begin{Bmatrix} \Omega & l_b & l_r^{(a)} \\ 0 & 0 & 0 \end{Bmatrix}^2 \begin{Bmatrix} \kappa & l_r^{(a)} & l_r^{(a)} \\ \Omega & l_b & l_b \end{Bmatrix} \begin{Bmatrix} S_a & S_b & S_{ab} \\ \frac{1}{2} & S_P^{(b)} & S_b \\ S_P^{(a)} & \frac{1}{2} & S_a \end{Bmatrix} \end{Bmatrix}. \quad (19b) \end{aligned}$$

Next, the photoexcitation transitions for an atom that contains three open subshells in its initial state will be considered:

$$\begin{aligned} & \hbar\omega + |((((n_a l_a)^{q_a} : L_a S_a \gamma_a)(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab} S_{ab})(n_c l_c)^{q_c} : L_c S_c \gamma_c) L_{abc} S_{abc}\rangle \\ & \rightarrow |((((n_a l_a)^{q_a-1} : L_P^{(a)} S_P^{(a)} \gamma_P^{(a)})(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab}^{(P)} S_{ab}^{(P)})(n_c l_c)^{q_c} : L_c S_c \gamma_c) L_{abc}^{(P)} S_{abc}^{(P)} + |\varepsilon_r^{(a)} l_r^{(a)}\rangle. \quad (20) \end{aligned}$$

For the potential interactions between the excited electron and the subshell from which the electron originated [subshell ( $a$ )], one obtains, again [16],

$$\begin{aligned} \langle V^{N-1}(\dots((n_a l_a)^{q_a} : L_a S_a \gamma_a)(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab} S_{ab})(n_c l_c)^{q_c} : L_c S_c \gamma_c) L_{abc} S_{abc}; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle \\ = \langle V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle . \end{aligned} \quad (21a)$$

For the potential interactions between the excited electron and subshell ( $b$ ), one obtains [16]

$$\begin{aligned} \langle V^{N-1}(\dots((n_a l_a)^{q_a} : L_a S_a \gamma_a)(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab} S_{ab})(n_c l_c)^{q_c} : L_c S_c \gamma_c) L_{abc} S_{abc}; (n_b l_b, \epsilon_r^{(a)} l_r^{(a)}) \rangle \\ = \langle V^{N-1}((n_a l_a)^{q_a} : L_a S_a \gamma_a)(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab} S_{ab}; (n_b l_b, \epsilon_r^{(a)} l_r^{(a)}) \rangle . \end{aligned} \quad (21b)$$

Equation (21b) demonstrates that Eq. (19b) is also a general result for two subshells that are coupled together.

Finally, for more complicated couplings and interactions in the initial state of the atom, the  $\langle V^{N-1} \rangle$  potential is obtained by a simple recoupling transformation over the initial state of the atom. For example, the potential interaction between the excited electron and subshell ( $c$ ) for the transition depicted in Eq. (20) can be written as [16]

$$\begin{aligned} \langle V^{N-1}(\dots((n_a l_a)^{q_a} : L_a S_a \gamma_a)(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab} S_{ab})(n_c l_c)^{q_c} : L_c S_c \gamma_c) L_{abc} S_{abc}; (n_c l_c, \epsilon_r^{(a)} l_r^{(a)}) \rangle \\ = \sum_{L_{ac}, S_{ac}} [L_{ab}, S_{ab}, L_{ac}, S_{ac}] \begin{Bmatrix} L_b & L_{ab} & L_a \\ L_c & L_{ac} & L_{abc} \end{Bmatrix}^2 \begin{Bmatrix} S_b & S_{ab} & S_a \\ S_c & S_{ac} & S_{abc} \end{Bmatrix}^2 \\ \times \langle V^{N-1}((n_a l_a)^{q_a} : L_a S_a \gamma_a)(n_c l_c)^{q_c} : L_c S_c \gamma_c) L_{ac} S_{ac}; (n_c l_c, \epsilon_r^{(a)} l_r^{(a)}) \rangle . \end{aligned} \quad (21c)$$

Equation (21c), again, displays the general nature of the result derived in Eq. (19b).

The extension to atoms with four or more open subshells in the initial state is obvious.

Next we examine some of the analytic properties of the algorithm that is presented in Eq. (9c). A definition of an average  $\langle V^{N-1} \rangle$  potential can be arrived at by using as weighting factors the  $L$  and  $S$  degeneracies of the initial-state configuration, and by normalizing over the number of electron pairs that are interacting:

$$\langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} l_r^{(a)})_{av} \rangle = \frac{\sum_{\gamma_a, L_a, S_a} [L_a, S_a] \langle V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle}{(q_a - 1) \sum_{\gamma_a, L_a, S_a} [L_a, S_a]} , \quad (22)$$

and

$$\langle V^{N-1}(n_b l_b; \epsilon_r^{(a)} l_r^{(a)})_{av} \rangle = \frac{\sum_{L_{ab}, S_{ab}} [L_{ab}, S_{ab}] \langle V^{N-1}(\dots((n_a l_a)^{q_a} : L_a S_a \gamma_a)(n_b l_b)^{q_b} : L_b S_b \gamma_b) L_{ab} S_{ab}; (n_b l_b, \epsilon_r^{(a)} l_r^{(a)}) \rangle}{(q_b) \sum_{L_{ab}, S_{ab}} [L_{ab}, S_{ab}]} . \quad (23)$$

With the definitions that are shown above and for all initial-state configurations and couplings, one obtains [16]

$$\begin{aligned} \langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} l_r^{(a)})_{av} \rangle &= \frac{2[l_a]}{(4l_a + 1)} \left[ F^0(n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \right. \\ &\quad \left. - \frac{1}{2} \sum_{\Omega} \begin{Bmatrix} l_a & \Omega & l_r^{(a)} \\ 0 & 0 & 0 \end{Bmatrix}^2 G^{\Omega}(n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \right] \\ &+ \sum_{\kappa} \frac{1}{(4l_a + 1)} [l_a, l_r^{(a)}] \begin{Bmatrix} l_r^{(a)} & l_r^{(a)} & \kappa \\ l_a & l_a & 1 \end{Bmatrix} \begin{Bmatrix} l_a & \kappa & l_a \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} l_r^{(a)} & \kappa & l_r^{(a)} \\ 0 & 0 & 0 \end{Bmatrix} F^{\kappa}(n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \\ &+ \frac{2}{3(4l_a + 1)} [l_a, l_r^{(a)}] \begin{Bmatrix} l_a & 1 & l_r^{(a)} \\ 0 & 0 & 0 \end{Bmatrix}^2 G^1(n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) , \end{aligned} \quad (24)$$

and [16]

$$\langle V^{N-1}(n_b l_b; \epsilon_r^{(a)} l_r^{(a)})_{av} \rangle = F^0(n_b l_b, \epsilon_r^{(a)} l_r^{(a)}) - \frac{1}{2} \sum_{\Omega} \begin{Bmatrix} l_b & \Omega & l_r^{(a)} \\ 0 & 0 & 0 \end{Bmatrix}^2 G^{\Omega}(n_b l_b, \epsilon_r^{(a)} l_r^{(a)}) . \quad (25)$$

Notice that one of the important differences between the average  $\langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} I_r^{(a)})_{av} \rangle$  and a Slater average for non-equivalent electrons is the possibility of a positive coefficient for the exchange term  $G^1(n_a l_a; \epsilon_r^{(a)} I_r^{(a)})$ . In fact, a quick analysis of Eq. (24) demonstrates that the coefficient of the exchange term  $G^1(n_a l_a; \epsilon_r^{(a)} I_r^{(a)})$  in  $\langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} I_r^{(a)})_{av} \rangle$  will be negative only if  $I_r^{(a)} = 0$ .

Equations (24) and (25) represent normalized results for the case when the atom consists initially of closed subshells. In this case, the singly excited  $LS$ -coupled channel is uniquely determined:

$$\hbar\omega + |(n_a l_a)^{4l_a+2}; L=0, S=0\rangle \rightarrow |(((n_a l_a)^{4l_a+1}; l_a, \frac{1}{2}) \epsilon_r^{(a)} I_r^{(a)})^1 P\rangle . \quad (26a)$$

Equation (24) represents the following identity:

$$\begin{aligned} \langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} I_r^{(a)})_{av} \rangle &= \frac{\langle V^{(N-1)}(n_a l_a)^{4l_a+2}; 0, 0; (n_a l_a, \epsilon_r^{(a)} I_r^{(a)}) \rangle}{(4l_a + 1)} \\ &= \frac{\langle (((n_a l_a)^{4l_a+1}; l_a, \frac{1}{2}) \epsilon_r^{(a)} I_r^{(a)})^1 P | r_{12}^{-1} | (((n_a l_a)^{4l_a+1}; l_a, \frac{1}{2}) \epsilon_r^{(a)} I_r^{(a)})^1 P \rangle}{(4l_a + 1)} , \end{aligned} \quad (26b)$$

where the equality in Eq. (26b) is only over the  $(n_a l_a, \epsilon_r^{(a)} I_r^{(a)})$  interaction. That is, the value of the matrix element  $\langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} I_r^{(a)})_{av} \rangle$  is equal to the excited orbital potential for transitions from a closed subshell, divided by the number of electron pairs that are interacting:  $4l_a + 1$ . The value of the matrix element  $\langle V^{N-1}(n_b l_b; \epsilon_r^{(a)} I_r^{(a)})_{av} \rangle$  is equal to the Slater average for nonequivalent electrons.

In special cases, for transitions from a subshell with a single electron [16],

$$\langle V^{N-1}(n_a l_a; l_a \frac{1}{2}; (n_a l_a, \epsilon_r^{(a)} I_r^{(a)})) \rangle = 0 , \quad (27)$$

for transitions from a subshell that has one less electron than a closed subshell [16],

$$\langle V^{N-1}(n_a l_a)^{4l_a+1}; l_a \frac{1}{2}; (n_a l_a, \epsilon_r^{(a)} I_r^{(a)}) \rangle = (4l_a) \langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} I_r^{(a)})_{av} \rangle , \quad (28)$$

for transitions from a closed subshell [16],

$$\langle V^{N-1}(n_a l_a)^{4l_a+2}; 0, 0; (n_a l_a, \epsilon_r^{(a)} I_r^{(a)}) \rangle = (4l_a + 1) \langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} I_r^{(a)})_{av} \rangle , \quad (29)$$

for the interaction between two subshells, with one subshell closed [16],

$$\langle V^{N-1}(((n_a l_a)^{4l_a+2}; 0, 0)(n_b l_b)^{q_b}; L_b S_b \gamma_b) L_b S_b; (n_b l_b, \epsilon_r^{(a)} I_r^{(a)}) \rangle = q_b \langle V^{N-1}(n_b l_b; \epsilon_r^{(a)} I_r^{(a)})_{av} \rangle , \quad (30)$$

$$\langle V^{N-1}(((n_a l_a)^{q_a}; L_a S_a \gamma_a)(n_b l_b)^{4l_b+2}; 0, 0) L_a S_a; (n_b l_b, \epsilon_r^{(a)} I_r^{(a)}) \rangle = 2[l_b] \langle V^{N-1}(n_b l_b; \epsilon_r^{(a)} I_r^{(a)})_{av} \rangle , \quad (31)$$

and for open subshells that are coupled to a single  $s$  electron in the initial state [16],

$$\begin{aligned} \langle V^{N-1}(((n_a l_a)^{q_a}; L_a S_a \gamma_a)(n_b l_b = s); 0 \frac{1}{2}) L_a S_a \pm \frac{1}{2}; (n_b s, \epsilon_r^{(a)} I_r^{(a)}) \rangle \\ = F^0(n_b s, \epsilon_r^{(a)} I_r^{(a)}) - \frac{1}{2q_a [l_r^{(a)}]} (q_a - 1 \pm [S_a]) G^{l_r^{(a)}}(n_b s, \epsilon_r^{(a)} I_r^{(a)}) , \end{aligned} \quad (32)$$

and [16]

$$\begin{aligned} \langle V^{N-1}(((n_a l_a = s); 0 \frac{1}{2})(n_b l_b)^{q_b}; L_b S_b \gamma_b) L_b S_b \pm \frac{1}{2}; (n_b l_b, \epsilon_r^{(a)} I_r^{(a)} = p) \rangle \\ = q_b \left[ F^0(n_b l_b, \epsilon_r^{(a)} p) - \sum_{\Omega} \frac{1}{2q_b} \begin{bmatrix} l_b & \Omega & 1 \\ 0 & 0 & 0 \end{bmatrix}^2 (q_b - 1 \pm [S_b]) G^{\Omega}(n_b l_b, \epsilon_r^{(a)} p) \right] . \end{aligned} \quad (33)$$

Equation (28) utilizes the fact that a closed subshell minus one electron will have a unique  $LS$  coupling in the initial state:  $l_a, \frac{1}{2}$ . Therefore the  $\langle V^{N-1} \rangle$  potential for such an initial state, according to Eq. (22), will be the excited orbital potential for transitions from a closed subshell, multiplied by the scaling factor  $4l_a / (4l_a + 1)$ . Using Eq. (26b), this appears as

$$\begin{aligned} \langle V^{N-1}(n_a l_a)^{4l_a+1}; l_a \frac{1}{2}; (n_a l_a, \epsilon_r^{(a)} I_r^{(a)}) \rangle \\ = \frac{4l_a}{(4l_a + 1)} \langle V^{N-1}(n_a l_a)^{4l_a+2}; 0, 0; (n_a l_a, \epsilon_r^{(a)} I_r^{(a)}) \rangle \\ = \frac{4l_a}{(4l_a + 1)} \langle (((n_a l_a)^{4l_a+1}; l_a, \frac{1}{2}) \epsilon_r^{(a)} I_r^{(a)})^1 P | r_{12}^{-1} | (((n_a l_a)^{4l_a+1}; l_a, \frac{1}{2}) \epsilon_r^{(a)} I_r^{(a)})^1 P \rangle . \end{aligned} \quad (34)$$



The relationships that are indicated by Eqs. (22)–(25) are very powerful results, and are useful for the implementation of  $\langle V^{N-1} \rangle$ . For example, using Eq. (22), the definition of a correction to the average  $\langle V^{N-1} \rangle$  potential can be established:

$$\langle \Delta V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a ; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle = \langle V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a ; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle - (q_a - 1) \langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} l_r^{(a)})_{\text{av}} \rangle . \quad (35)$$

For conjugate configurations in the initial state, it has been proven that [16]

$$\langle \Delta V^{N-1}(n_a l_a)^{4l_a+2-q_a} : L_a S_a \gamma_a ; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle = \frac{q_a}{(4l_a+2-q_a)} \langle \Delta V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a ; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle . \quad (36)$$

Table I contains the values of  $\langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} l_r^{(a)})_{\text{av}} \rangle$  for  $l_a = s, p,$  and  $d$  electrons. Table II contains the values of  $\langle \Delta V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a ; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle$  for all of the initial-state  $p$  and  $d$  couplings up to and including half-filled subshells. The contributions to the potential for the  $s^q$  configurations are determined from Eqs. (27)–(29).

For the case  $q_a \leq 2l_a + 1$ , the  $\langle V^{N-1} \rangle$  potential is given by

$$\langle V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a ; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle = (q_a - 1) \langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} l_r^{(a)})_{\text{av}} \rangle + \langle \Delta V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a ; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle , \quad (37)$$

which can be constructed from Tables I and II.

For the case  $q_a > 2l_a + 1$ , the  $\langle V^{N-1} \rangle$  potential is given by

$$\langle V^{N-1}(n_a l_a)^{q_a} : L_a S_a \gamma_a ; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle = (q_a - 1) \langle V^{N-1}(n_a l_a; \epsilon_r^{(a)} l_r^{(a)})_{\text{av}} \rangle + \frac{(4l_a + 2 - q_a)}{q_a} \langle \Delta V^{N-1}(n_a l_a)^{4l_a+2-q_a} : L_a S_a \gamma_a ; (n_a l_a, \epsilon_r^{(a)} l_r^{(a)}) \rangle . \quad (38)$$

again, which can be constructed from Tables I and II.

In the perturbation expansion of the dipole matrix elements, the diagrams which the  $\langle V^{N-1} \rangle$  potential does not cancel in the final state are shown in Fig. 2. In Fig. 2, an excited orbital has been labeled with the core index  $a$  in order to indicate an excitation into one of the unoccupied  $m_l^{(a)}$ , or valence, orbitals of the open subshell  $n_a l_a$ . These diagrams will occur only in open-shell systems. In order to determine the angular contribution from the diagrams in Fig. 2 to a particular  $LS$ -coupled final channel  $|F(I)\rangle$ , the following formula from perturbation theory can be used:

[angular contribution from the diagrams in Fig. 2 to the channel  $|F(I)\rangle$ ]

$$= \sum_J \langle F(I) | r_{12}^{-1} | F(J) \rangle \langle F(J) | Z_{\text{op}} | G(M_L) \rangle - \langle V^{N-1}(G); (nl, \epsilon l_f) \rangle \langle F(I) | Z_{\text{op}} | G(M_L) \rangle . \quad (39)$$

The analytic relationships discussed in this section make the  $\langle V^{N-1} \rangle$  potential very easy to apply. For example, let us consider the ground state of fluorine:  $[\text{He}]2s^2 2p^5$ . Let us suppose that we are interested in constructing the  $\langle V^{N-1} \rangle$  potential for the excited  $\epsilon d$  orbital for transitions from the  $2p$  subshell. According to Eq. (28), the  $\langle V^{N-1} \rangle$  contribution will be given by

$$\langle V^{N-1} 2p^5 : ^2P ; (2p, \epsilon d) \rangle = 4 \langle V^{N-1}(2p; \epsilon d)_{\text{av}} \rangle . \quad (40)$$

From Table I, therefore,

TABLE I. The  $\langle V^{N-1}(l_a; l_r^{(a)})_{\text{av}} \rangle$  contribution to the single-particle potential as defined in Eqs. (22) and (24) for  $l_a = s, p,$  and  $d$  electrons. The coefficients in this table were obtained by evaluating Eq. (14) for all  $s^q, p^q,$  and  $d^q$  initial-state configurations and couplings, and then performing the averaging procedure indicated in Eq. (22). The results were then checked against the analytic results indicated in Eq. (24). Notice that one of the important differences between the average  $\langle V^{N-1}(l_a; l_r^{(a)})_{\text{av}} \rangle$  and a Slater average for nonequivalent electrons is the possibility of a positive coefficient for the exchange term  $G^1(l_a, l_r^{(a)})$ .

$l_a$	$l_r^{(a)}$	$\langle V^{N-1}(l_a; l_r^{(a)})_{\text{av}} \rangle$					
		$F^0(l_a, l_r^{(a)})$	$G^1(l_a, l_r^{(1)})$	$F^2(l_a, l_r^{(a)})$	$G^3(l_a, l_r^{(a)})$	$F^4(l_a, l_r^{(a)})$	$G^5(l_a, l_r^{(a)})$
$s$	$p$	1	$\frac{1}{3}$	0	0	0	0
$p$	$s$	1	$-\frac{1}{15}$	0	0	0	0
$p$	$d$	1	$\frac{14}{75}$	$-\frac{1}{25}$	$-\frac{9}{175}$	0	0
$d$	$p$	1	$\frac{2}{27}$	$-\frac{1}{45}$	$-\frac{1}{21}$	0	0
$d$	$f$	1	$\frac{11}{63}$	$-\frac{8}{315}$	$-\frac{4}{189}$	$-\frac{2}{189}$	$-\frac{50}{2079}$

TABLE II. The  $\langle \Delta V^{N-1} l_a^{q_a} : L_a S_a \gamma_a ; (l_a, l_r^{(a)}) \rangle$  contribution to the single-particle potential as defined in Eq. (35) for  $l_a = p$  and  $d$  electrons up to and including half-filled subshells in the initial state. Equation (36) provides the relationship necessary to deduce  $\langle \Delta V^{N-1} l_a^{q_a} : L_a S_a \gamma_a ; (l_a, l_r^{(a)}) \rangle$  for the subshells that are more than half filled in the initial state. The general case  $l_a = s$  is covered by Eqs. (27)–(29) and Table I. The coefficients in this table were obtained by evaluating Eq. (14) for all  $p^q$  and  $d^q$  initial-state configurations and couplings, and then performing the subtraction indicated in Eq. (35). The relationship indicated in Eq. (36) was found to hold and served as a double check for all except the half-filled-subshell configurations. A further check on the coefficients is the identity  $\sum_{\gamma_a, L_a, S_a} [L_a, S_a] \langle \Delta V^{N-1} l_a^{q_a} : L_a S_a \gamma_a ; (l_a, l_r^{(a)}) \rangle = 0$ , which is a trivial result of Eqs. (22) and (35). The presubscript  $\gamma_a$  in the third column refer to Racah seniority numbers.

$l_a^{q_a}$	$l_r^{(a)}$	${}^{2S_a+1}L_a$	$\langle \Delta V^{N-1} l_a^{q_a} : L_a S_a \gamma_a ; (l_a, l_r^{(a)}) \rangle$		
			$G^1(l_a, l_r^{(a)})$	$F^2(l_a, l_r^{(a)})$	$G^3(l_a, l_r^{(a)})$
$p^2$	$s$	${}^3P$	$-\frac{4}{15}$	0	0
		${}^1D$	$\frac{6}{15}$	0	0
		${}^1S$	$\frac{6}{15}$	0	0
$p^3$	$s$	${}^4S$	$-\frac{8}{15}$	0	0
		${}^2D$	$\frac{2}{15}$	0	0
		${}^2P$	$\frac{2}{15}$	0	0
$p^2$	$d$	${}^3P$	$-\frac{4}{75}$	$-\frac{3}{50}$	$-\frac{27}{350}$
		${}^1D$	$\frac{9}{75}$	$\frac{3}{50}$	$\frac{27}{350}$
		${}^1S$	$-\frac{9}{75}$	$\frac{12}{50}$	$\frac{108}{350}$
$p^3$	$d$	${}^4S$	$-\frac{8}{75}$	$-\frac{3}{25}$	$-\frac{27}{175}$
		${}^2D$	$\frac{5}{75}$	0	0
		${}^2P$	$-\frac{3}{75}$	$\frac{2}{25}$	$\frac{18}{175}$
$d^2$	$p$	${}^3F$	$-\frac{10}{135}$	$-\frac{58}{630}$	$-\frac{20}{1470}$
		${}^3P$	$-\frac{10}{135}$	$\frac{77}{630}$	$-\frac{245}{1470}$
		${}^1G$	$\frac{44}{135}$	$\frac{50}{630}$	$\frac{88}{1470}$
		${}^1D$	$-\frac{19}{135}$	$-\frac{13}{630}$	$\frac{277}{1470}$
		${}^1S$	$-\frac{1}{135}$	$\frac{140}{630}$	$\frac{448}{1470}$
$d^3$	$p$	${}^4F$	$-\frac{40}{270}$	$-\frac{31}{315}$	$-\frac{65}{735}$
		${}^4P$	$-\frac{40}{270}$	$\frac{14}{315}$	$-\frac{140}{735}$
		${}^2H$	$\frac{68}{270}$	$-\frac{4}{315}$	$\frac{34}{735}$
		${}^2G$	$\frac{8}{270}$	$-\frac{19}{315}$	$\frac{79}{735}$
		${}^2F$	$\frac{32}{270}$	$\frac{41}{315}$	$-\frac{29}{735}$
		${}^2D$	$-\frac{1}{270}$	$\frac{35}{315}$	$\frac{112}{735}$
		${}^2D$	$-\frac{13}{270}$	$\frac{23}{315}$	$\frac{16}{735}$
		${}^2P$	$-\frac{58}{270}$	$-\frac{4}{315}$	$\frac{76}{735}$
		${}^2P$	$\frac{270}{270}$	$\frac{315}{315}$	$\frac{735}{735}$
$d^4$	$p$	${}^5D$	$-\frac{40}{180}$	$-\frac{35}{420}$	$-\frac{175}{980}$
		${}^3H$	$\frac{20}{180}$	$-\frac{23}{420}$	$\frac{5}{980}$
		${}^3G$	$\frac{5}{180}$	$-\frac{8}{420}$	$-\frac{10}{980}$
		${}^3F$	$\frac{2}{180}$	$\frac{22}{420}$	$\frac{32}{980}$
		${}^3F$	$-\frac{7}{180}$	$\frac{4}{420}$	$-\frac{22}{980}$
		${}^3D$	$-\frac{16}{180}$	$\frac{13}{420}$	$-\frac{31}{980}$
		${}^3P$	$-\frac{28}{180}$	$\frac{7}{420}$	$\frac{77}{980}$
		${}^2P$	$\frac{180}{180}$	$\frac{420}{420}$	$\frac{980}{980}$

TABLE II. (Continued).

$\langle \Delta V^{N-1} l_a^{q_a} : L_a S_a \gamma_a ; (l_a, l_r^{(a)}) \rangle$									
$l_a^{q_a}$	$l_r^{(a)}$	$\frac{2S_a+1}{\gamma_a} L_a$	$G^1(l_a, l_r^{(a)})$	$F^2(l_a, l_r^{(a)})$	$G^3(l_a, l_r^{(a)})$				
$d^4$	$p$	$\frac{3}{4}P$	$\frac{-22}{180}$	$\frac{19}{420}$	$\frac{-37}{980}$				
		$\frac{1}{4}I$	$\frac{50}{180}$	$\frac{-17}{420}$	$\frac{95}{980}$				
		$\frac{1}{2}G$	$\frac{14}{180}$	$\frac{10}{420}$	$\frac{164}{980}$				
		$\frac{1}{4}G$	$\frac{17}{180}$	$\frac{16}{420}$	$\frac{62}{980}$				
		$\frac{1}{4}F$	$\frac{5}{180}$	$\frac{28}{420}$	$\frac{50}{980}$				
		$\frac{1}{2}D$	$\frac{14}{180}$	$\frac{73}{420}$	$\frac{59}{980}$				
		$\frac{1}{4}D$	$\frac{-4}{180}$	$\frac{37}{420}$	$\frac{41}{980}$				
		$\frac{1}{0}S$	$\frac{-1}{180}$	$\frac{70}{420}$	$\frac{224}{980}$				
		$\frac{1}{0}S$	$\frac{-13}{180}$	$\frac{46}{420}$	$\frac{32}{980}$				
		$d^5$	$p$	$\frac{6}{5}S$	$\frac{-200}{675}$	$\frac{-175}{1575}$	$\frac{-875}{3675}$		
				$\frac{4}{5}G$	$\frac{-20}{675}$	$\frac{-85}{1575}$	$\frac{-245}{3675}$		
				$\frac{4}{3}F$	$\frac{-20}{675}$	$\frac{23}{1575}$	$\frac{-245}{3675}$		
$\frac{4}{5}D$	$\frac{-83}{675}$			$\frac{-22}{1575}$	$\frac{-308}{3675}$				
$\frac{4}{3}P$	$\frac{-155}{675}$			$\frac{-112}{1575}$	$\frac{70}{3675}$				
$\frac{2}{5}I$	$\frac{133}{675}$			$\frac{-76}{1575}$	$\frac{178}{3675}$				
$\frac{2}{3}H$	$\frac{61}{675}$			$\frac{-58}{1575}$	$\frac{376}{3675}$				
$\frac{2}{3}G$	$\frac{106}{675}$			$\frac{167}{1575}$	$\frac{-29}{3675}$				
$\frac{2}{5}G$	$\frac{34}{675}$			$\frac{23}{1575}$	$\frac{79}{3675}$				
$\frac{2}{3}F$	$\frac{-74}{675}$			$\frac{-85}{1575}$	$\frac{511}{3675}$				
$\frac{2}{5}F$	$\frac{-2}{675}$			$\frac{59}{1575}$	$\frac{43}{3675}$				
$\frac{2}{1}D$	$\frac{-2}{675}$			$\frac{140}{1575}$	$\frac{448}{3675}$				
$\frac{2}{3}D$	$\frac{-20}{675}$			$\frac{104}{1575}$	$\frac{160}{3675}$				
$\frac{2}{5}D$	$\frac{-29}{675}$			$\frac{86}{1575}$	$\frac{16}{3675}$				
$\frac{2}{3}P$	$\frac{61}{675}$			$\frac{320}{1575}$	$\frac{-254}{3675}$				
$\frac{2}{5}S$	$\frac{-56}{675}$			$\frac{113}{1575}$	$\frac{-11}{3675}$				
$\langle \Delta V^{N-1} l_a^{q_a} : L_a S_a \gamma_a ; (l_a, l_r^{(a)}) \rangle$									
$l_a^{q_a}$	$l_r^{(a)}$			$\frac{2S_a+1}{\gamma_a} L_a$	$G^1(l_a, l_r^{(a)})$	$F^2(l_a, l_r^{(a)})$	$G^3(l_a, l_r^{(a)})$	$F^4(l_a, l_r^{(a)})$	$G^5(l_a, l_r^{(a)})$
$d^2$	$f$			$\frac{3}{4}F$	$\frac{20}{2205}$	$\frac{-232}{2205}$	$\frac{-490}{6615}$	$\frac{5}{1323}$	$\frac{125}{14553}$
				$\frac{3}{2}P$	$\frac{-280}{2205}$	$\frac{308}{2205}$	$\frac{560}{6615}$	$\frac{-70}{1323}$	$\frac{-1750}{14553}$
		$\frac{1}{2}G$	$\frac{368}{2205}$	$\frac{200}{2205}$	$\frac{414}{6615}$	$\frac{15}{1323}$	$\frac{375}{14553}$		
		$\frac{1}{2}D$	$\frac{-178}{2205}$	$\frac{-52}{2205}$	$\frac{176}{6615}$	$\frac{50}{1323}$	$\frac{1250}{14553}$		
		$\frac{1}{0}S$	$\frac{-322}{2205}$	$\frac{560}{2205}$	$\frac{644}{6615}$	$\frac{140}{1323}$	$\frac{3500}{14553}$		
		$d^3$	$f$	$\frac{4}{3}F$	$\frac{-80}{2205}$	$\frac{-248}{2205}$	$\frac{-1680}{19845}$	$\frac{-60}{3969}$	$\frac{-1500}{43659}$
$\frac{4}{3}P$	$\frac{-280}{2205}$			$\frac{112}{2205}$	$\frac{420}{19845}$	$\frac{-210}{3969}$	$\frac{-5250}{43659}$		
$\frac{2}{3}H$	$\frac{388}{2205}$			$\frac{-32}{2205}$	$\frac{-228}{19845}$	$\frac{60}{3969}$	$\frac{1500}{43659}$		
$\frac{2}{3}G$	$\frac{128}{2205}$			$\frac{-152}{2205}$	$\frac{-568}{19845}$	$\frac{110}{3969}$	$\frac{2750}{43659}$		
$\frac{2}{3}F$	$\frac{-8}{2205}$			$\frac{328}{2205}$	$\frac{2088}{19845}$	$\frac{-90}{3969}$	$\frac{-2250}{43659}$		
$\frac{2}{1}D$	$\frac{-161}{2205}$			$\frac{280}{2205}$	$\frac{966}{19845}$	$\frac{210}{3969}$	$\frac{5250}{43659}$		
$\frac{2}{3}D$	$\frac{-173}{2205}$			$\frac{184}{2205}$	$\frac{1518}{19845}$	$\frac{-30}{3969}$	$\frac{-750}{43659}$		
$\frac{2}{3}P$	$\frac{-298}{2205}$			$\frac{-32}{2205}$	$\frac{528}{19845}$	$\frac{60}{3969}$	$\frac{1500}{43659}$		

TABLE II. (Continued).

$l_a^{q_a}$	$l_r^{(a)}$	$2S_a + 1$ $\gamma_a L_a$	$\langle \Delta V^{N-1} l_a^{q_a} : L_a S_a \gamma_a ; (l_a, l_r^{(a)}) \rangle$						
			$G^1(l_a, l_r^{(a)})$	$F^2(l_a, l_r^{(a)})$	$G^3(l_a, l_r^{(a)})$	$F^4(l_a, l_r^{(a)})$	$G^5(l_a, l_r^{(a)})$		
$d^4$	$f$	${}^5_4D$	$\frac{-140}{1470}$	$\frac{-70}{735}$	$\frac{-525}{6615}$	$\frac{-105}{2646}$	$\frac{-2625}{29106}$		
		${}^3_4H$	$\frac{160}{1470}$	$\frac{-46}{735}$	$\frac{-285}{6615}$	$\frac{15}{2646}$	$\frac{375}{29106}$		
		${}^3_4G$	$\frac{45}{1470}$	$\frac{-16}{735}$	$\frac{-65}{6615}$	$\frac{-10}{2646}$	$\frac{-250}{29106}$		
		${}^3_2F$	$\frac{-38}{1470}$	$\frac{44}{735}$	$\frac{99}{6615}$	$\frac{45}{2646}$	$\frac{1125}{29106}$		
		${}^3_4F$	$\frac{-47}{1470}$	$\frac{8}{735}$	$\frac{111}{6615}$	$\frac{-30}{2646}$	$\frac{-750}{29106}$		
		${}^3_4D$	$\frac{-116}{1470}$	$\frac{26}{735}$	$\frac{243}{6615}$	$\frac{-45}{2646}$	$\frac{-1125}{29106}$		
		${}^3_2P$	$\frac{-168}{1470}$	$\frac{14}{735}$	$\frac{14}{6615}$	$\frac{70}{2646}$	$\frac{1750}{29106}$		
		${}^3_4P$	$\frac{-162}{1470}$	$\frac{38}{735}$	$\frac{331}{6615}$	$\frac{-55}{2646}$	$\frac{-1375}{29106}$		
		${}^1_4I$	$\frac{310}{1470}$	$\frac{-34}{735}$	$\frac{-165}{6615}$	$\frac{75}{2646}$	$\frac{1875}{29106}$		
		${}^1_2G$	$\frac{54}{1470}$	$\frac{20}{735}$	$\frac{63}{6615}$	$\frac{135}{2646}$	$\frac{3375}{29106}$		
		${}^1_4G$	$\frac{57}{1470}$	$\frac{32}{735}$	$\frac{319}{6615}$	$\frac{20}{2646}$	$\frac{500}{29106}$		
		${}^1_4F$	$\frac{-35}{1470}$	$\frac{56}{735}$	$\frac{495}{6615}$	0	0		
		${}^1_2D$	$\frac{-86}{1470}$	$\frac{146}{735}$	$\frac{798}{6615}$	$\frac{30}{2646}$	$\frac{750}{29106}$		
		${}^1_4D$	$\frac{-104}{1470}$	$\frac{74}{735}$	$\frac{627}{6615}$	$\frac{-15}{2646}$	$\frac{-375}{29106}$		
		${}^1_0S$	$\frac{-161}{1470}$	$\frac{140}{735}$	$\frac{483}{6615}$	$\frac{210}{2646}$	$\frac{5250}{29106}$		
		${}^1_4S$	$\frac{-173}{1470}$	$\frac{92}{735}$	$\frac{759}{6615}$	$\frac{-30}{2646}$	$\frac{-750}{29106}$		
		$d^5$	$f$	${}^6_5S$	$\frac{-1400}{11025}$	$\frac{-1400}{11025}$	$\frac{-3500}{33075}$	$\frac{-70}{1323}$	$\frac{-1750}{14553}$
				${}^4_5G$	$\frac{160}{11025}$	$\frac{-680}{11025}$	$\frac{-1420}{33075}$	$\frac{-20}{1323}$	$\frac{-500}{14553}$
				${}^4_3F$	$\frac{-320}{11025}$	$\frac{184}{11025}$	$\frac{-260}{33075}$	$\frac{-16}{1323}$	$\frac{-400}{14553}$
				${}^4_5D$	$\frac{-806}{11025}$	$\frac{-176}{11025}$	$\frac{-188}{33075}$	$\frac{-34}{1323}$	$\frac{-850}{14553}$
${}^4_3P$	$\frac{-1190}{11025}$			$\frac{-896}{11025}$	$\frac{-1820}{33075}$	$\frac{14}{1323}$	$\frac{350}{14553}$		
${}^2_5I$	$\frac{1786}{11025}$			$\frac{-608}{11025}$	$\frac{-1052}{33075}$	$\frac{20}{1323}$	$\frac{500}{14553}$		
${}^2_3H$	$\frac{922}{11025}$			$\frac{-464}{11025}$	$\frac{-1004}{33075}$	$\frac{44}{1323}$	$\frac{1100}{14553}$		
${}^2_3G$	$\frac{412}{11025}$			$\frac{1336}{11025}$	$\frac{2316}{33075}$	$\frac{-6}{1323}$	$\frac{-150}{14553}$		
${}^2_5G$	$\frac{268}{11025}$			$\frac{184}{11025}$	$\frac{884}{33075}$	$\frac{-2}{1323}$	$\frac{-50}{14553}$		
${}^2_3F$	$\frac{-428}{11025}$			$\frac{-680}{11025}$	$\frac{-884}{33075}$	$\frac{50}{1323}$	$\frac{1250}{14553}$		
${}^2_5F$	$\frac{-284}{11025}$			$\frac{472}{11025}$	$\frac{1588}{33075}$	$\frac{-10}{1323}$	$\frac{-250}{14553}$		
${}^2_1D$	$\frac{-644}{11025}$			$\frac{1120}{11025}$	$\frac{1288}{33075}$	$\frac{56}{1323}$	$\frac{1400}{14553}$		
${}^2_3D$	$\frac{-680}{11025}$			$\frac{832}{11025}$	$\frac{1840}{33075}$	$\frac{8}{1323}$	$\frac{200}{14553}$		
${}^2_5D$	$\frac{-698}{11025}$			$\frac{688}{11025}$	$\frac{2116}{33075}$	$\frac{-16}{1323}$	$\frac{-400}{14553}$		
${}^2_3P$	$\frac{-758}{11025}$			$\frac{2560}{11025}$	$\frac{4876}{33075}$	$\frac{-40}{1323}$	$\frac{-1000}{14553}$		
${}^2_5S$	$\frac{-1112}{11025}$			$\frac{904}{11025}$	$\frac{2644}{33075}$	$\frac{-22}{1323}$	$\frac{-550}{14553}$		

$$\langle V^{N-1} 2p^5 : {}^2P; (2p, \epsilon d) \rangle = 4[F^0(2p, \epsilon d) + \frac{14}{75} G^1(2p, \epsilon d) - \frac{1}{25} F^2(2p, \epsilon d) - \frac{9}{175} G^3(2p, \epsilon d)], \quad (41a)$$

or

$$\langle V^{N-1} 2p^5 : {}^2P; (2p, \epsilon d) \rangle = 4F^0(2p, \epsilon d) + \frac{56}{75} G^1(2p, \epsilon d) - \frac{4}{25} F^2(2p, \epsilon d) - \frac{36}{175} G^3(2p, \epsilon d). \quad (41b)$$

Notice that these angular coefficients are also valid for the  $\hbar\omega + 3p \rightarrow \epsilon d$  excitations in chlorine, with the initial state  $[\text{Ne}]3s^2 3p^5$ . Comparison between the results of Eq. (41b) and the  ${}_Q \langle V^{N-1} \rangle$  angular coefficients for chlorine published in the QCK paper show that

$$\max \left[ \frac{|\langle V^{N-1} 3p^5 : {}^2P; (3p, \epsilon d) \rangle - {}_Q \langle V^{N-1} 3p^5 : {}^2P; (3p, \epsilon d) \rangle|}{|{}_Q \langle V^{N-1} 3p^5 : {}^2P; (3p, \epsilon d) \rangle|} \right] \approx 1\%, \quad (42)$$

consistent with the results of Eq. (11).

Next, we will consider the more complicated case of the ground state of carbon:  $[\text{He}](2s^2 2p^2)^3P$ . Again, let us suppose that we are interested in constructing the  $\langle V^{N-1} \rangle$  potential for the excited  $\epsilon d$  orbital for transitions from the  $2p$  subshell. According to Eq. (37), the  $\langle V^{N-1} \rangle$  contribution will be given by

$$\langle V^{N-1} 2p^2:3P; (2p, \epsilon d) \rangle = \langle V^{N-1}(2p; \epsilon d)_{\text{av}} \rangle + \langle \Delta V^{N-1} 2p^2:3P; (2p, \epsilon d) \rangle. \quad (43)$$

From Tables I and II, we obtain

$$\begin{aligned} \langle V^{N-1} 2p^2:3P; (2p, \epsilon d) \rangle = & [F^0(2p, \epsilon d) + \frac{14}{75} G^1(2p, \epsilon d) - \frac{1}{25} F^2(2p, \epsilon d) - \frac{9}{175} G^3(2p, \epsilon d)] \\ & + [ \frac{-4}{75} G^1(2p, \epsilon d) - \frac{3}{50} F^2(2p, \epsilon d) - \frac{27}{350} G^3(2p, \epsilon d) ], \end{aligned} \quad (44a)$$

or

$$\langle V^{N-1} 2p^2:3P; (2p, \epsilon d) \rangle = F^0(2p, \epsilon d) + \frac{2}{15} G^1(2p, \epsilon d) - \frac{1}{10} F^2(2p, \epsilon d) - \frac{9}{70} G^2(2p, \epsilon d). \quad (44b)$$

Finally, we will consider an atom with a ground-state configuration which is conjugate to the ground-state configuration of carbon: we will consider transitions from the ground state of oxygen  $[\text{He}](2s^2 2p^4)^3P$ . Again, we suppose that we are interested in constructing the  $\langle V^{N-1} \rangle$  potential for the excited  $\epsilon d$  orbital for transitions from the  $2p$  subshell. According to Eq. (38), the  $\langle V^{N-1} \rangle$  contribution in this case will be given by

$$\langle V^{N-1} 2p^4:3P; (2p, \epsilon d) \rangle = 3 \langle V^{N-1}(2p; \epsilon d)_{\text{av}} \rangle + \frac{2}{4} \langle \Delta V^{N-1} 2p^2:3P; (2p, \epsilon d) \rangle. \quad (45)$$

From Tables I and II, again, we obtain

$$\begin{aligned} \langle V^{N-1} 2p^4:3P; (2p, \epsilon d) \rangle = & 3[F^0(2p, \epsilon d) + \frac{14}{75} G^1(2p, \epsilon d) - \frac{1}{25} F^2(2p, \epsilon d) - \frac{9}{175} G^3(2p, \epsilon d)] \\ & + \frac{1}{2} [ \frac{-4}{75} G^1(2p, \epsilon d) - \frac{3}{50} F^2(2p, \epsilon d) - \frac{27}{350} G^3(2p, \epsilon d) ], \end{aligned} \quad (46a)$$

or

$$\begin{aligned} \langle V^{N-1} 2p^4:3P; (2p, \epsilon d) \rangle = & 3F^0(2p, \epsilon d) + \frac{8}{15} G^1(2p, \epsilon d) \\ & - \frac{3}{20} F^2(2p, \epsilon d) \\ & - \frac{27}{140} G^3(2p, \epsilon d). \end{aligned} \quad (46b)$$

In Eqs. (40)–(41b) and Eqs. (43)–(46b), we have identified the angular factors that would be used for the calculation of the photoexcited  $\epsilon d$  orbitals and that are solely determined by the initial-state couplings:  $[\text{He}]2s^2 2p^5$ ,  $[\text{He}](2s^2 2p^2)^3P$ , and  $[\text{He}](2s^2 2p^4)^3P$ .

#### IV. CONCLUSIONS

An attempt has been made to define a potential for the calculation of basis sets of orbitals that can be used in photoexcitation problems. The algorithm for the construction of the potential was defined in order to be consistent with the perturbation expansion of the dipole polarizability.

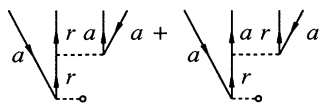


FIG. 2. The lowest-order diagrams that contribute to the perturbation series of an exact dipole matrix element and that are not taken into account by using the potential defined in this paper. These diagrams are peculiar to atoms that contain open subshells in their initial states, since the existence of both the hole orbital  $a$  and the particle orbital  $a$  indicates that the  $n_a l_a$  subshell is not completely filled in the initial state. The corrections to an exact dipole matrix element represented by the diagrams shown in this figure and Eq. (39) are expected to be small for problems that involve single photoexcitation processes.

The two tables in this paper contain the angular coefficients associated with

$$\langle V^{(N-1)}(nl)^q:LS\gamma, (nl, \epsilon(l \pm 1)) \rangle,$$

extending over 91 separate initial-state couplings. Additionally, the analytic results that are contained in Eqs. (14), (19b), (21c), and (27)–(33) allow one to treat arbitrarily complex initial-state configurations. Access to the tables simplifies the use of this potential. With the rules that are provided in Eqs. (27)–(33), (37), and (38), one can easily construct the potential for the excited orbitals such that the first-order corrections to the dipole polarizability are cancelled, as shown in Fig. 1.

As demonstrated in Eqs. (11) and (42), the quantitative closeness of  $Q \langle V^{N-1} \rangle$  and the  $\langle V^{N-1} \rangle$  potential defined in this paper, and the fact that excellent convergence has been obtained in the past using  $Q \langle V^{N-1} \rangle$  indicates that one should expect comparable convergence using the  $\langle V^{N-1} \rangle$  potential introduced here.

It is hoped that the simplicity of the solution presented in this paper will motivate investigations into other problems where the interplay between electron-correlation effects and the choice of the potential in the final state can be significant for the convergence of a calculation.

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