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Many-body theory of atomic transitions*

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Hartree-Fock equations for transition matrices are formulated as an extension of the ordinary theory of atomic spectra. These equations form a hierarchy which may be subjected to various truncations. Some of the truncations are identified as equivalent to different forms of many-body theories (random-phase approximation, time-dependent Hartree-Fock, many-body perturbation theory, etc.). Thereby we connect the modern many-body treatments more explicitly with the Condon-Shortley-Racah tradition of spectral theory and provide physical interpretations of various approximations. Spin and angular variables are factored out at the outset by angular-momentum techniques. The problem then takes the form of a system of integro-differential equations for radial wave functions, which affords conceptual and computational advantages. The correlations that are characteristically studied by many-body techniques are seen to be confined to short radial distances and could accordingly be treated by R-matrix procedures.

I. INTRODUCTION

Many-body theory techniques have proved themselves in recent years by accounting for previously unexplained major features of atomic spectra. Particularly striking was the success of Amusia and co-workers in explaining large departures of the Ar and Xe oscillator-strength distributions from the predictions of single-particle models.[1,2] Three such lines of work have proceeded rather independently, namely:

(i) The RPA (random-phase approximation) approach, originating from the physics of condensed matter and used extensively in nuclear physics, has been applied to the photoionization of atoms by Amusia and Cherepkov[2] as well as by Wendin[3,4] and more recently by others.[5,6] [The term "RPA" is meant in this paper to include the treatment which is called RPAE (RPA with exchange) by Amusia and others.] Applications to the discrete spectra of molecules have been made recently by McKoy and co-workers.[7] The theoretical background is described in the nuclear treatises by Brown[8] and Thouless[9] and in an article by Rowe.[10] Use of a basis of independent-particle states, truncated on the high-energy side, leads to computation of large algebraic systems.

(ii) The time-dependent Hartree-Fock (TDHF) approach has been applied to calculate the dynamical polarizability and other response functions of light atoms, primarily by Dalgarno and Victor,[11] the results prior to 1973 being reviewed by Jamieson.[12] The basic equations of this approach and of the RPA are known to be equivalent, but the procedural details of the two methods and their interpretation have proved difficult to compare. TDHF calculations consist of solving coupled integro-differential equations for single-electron radial wave functions. Because of the basic equivalence of RPA and TDHF procedures,[12] remarks concerning the RPA in this paper will often apply by implication to the TDHF as well.

(iii) The many-body perturbation methods (MBPT) originate from Brueckner's and Goldstone's works in nuclear physics[13] and have been applied by Kelly's and other groups initially to the calculation of correlation energies and of other ground-state properties[14,15] but increasingly also to photoabsorption.[16-19] These methods are related, but not equivalent, to the RPA and TDHF. Calculations have been made mostly by solving algebraic systems but have been reduced more recently to solving integro-differential equations.[18,19]

As these approaches were implemented by different groups of workers using different techniques, they have remained rather disconnected, in that even practitioners of the field experience difficulty with their intercomparisons. They also remained disconnected from the standard Condon-Shortley-Racah approach of theoretical spectroscopy. The resulting mismatch has hindered the transfer of experience and intuition between different approaches and, consequently, the efforts to pinpoint and to overcome or bypass the limitations of each of them. Efforts to extend their ranges of application have been laborious but expanding rapidly in recent months.[20]

Accordingly, we have endeavored to identify a treatment and a point of view that would encompass the various approaches and would facilitate the analysis and illustration of their relationships as well as their progressive extension. The Green's-function formalism is a candidate for this purpose, because it deals with any particular problem starting from a formal analytical solution whose evaluation can proceed flexibly by alternative approximate expansions.[9,21] We have preferred, however, to keep closer to the more traditional theory of spectra, utilizing its wave-mechanical representation, angular-momentum algebra, and configuration-mixing (or, rather, channel-mixing[22,23]) procedures, which provide for unlimited extension as appropriate to any specific problem.

This framework will be extended in Sec. II to include an element foreign to traditional spectroscopy but common to all the many-body approaches, namely, the simultaneous treatment of the initial and final states of a transition. The extension will lead us to a hierarchy of equations whose approximate solution is to be achieved by truncation procedures. One such truncation reduces the equations to the homogeneous form of the TDHF equations [Eq. (V18) of Ref. 8]. Section III will connect various forms of many-body theory to our equations. In the development of our open-ended hierarchy of equations we shall find that the appearance of apparent inconsistencies serves as an indicator of the effects of truncation.

To make our presentation reasonably self-contained, some material other than our own has been included. For simplicity, we shall deal mostly with the simple example of Ar photoionization from the ground-state $3p$ shell to d states only.

Finally, two points may be stressed to clarify the application of many-body treatments to atomic spectra:

(a) Many-body treatments have dealt very successfully with a *particular class* of electron-correlation effects, namely, those in which ground- and excited-state correlations are strongly coupled. Yet they need not prove either useful or adequate in other circumstances. (Indeed, A. F. Starace kindly informs us that the coupling of ground- and excited-state correlations turns out to be weak in the photoabsorption of Cl, in contrast to that of Ar from which Cl differs by a single $3p$ electron; the loss of coupling stems from the geometrical averaging inherent in the addition of the transition angular momentum to the nonzero angular momentum of the open-shell Cl ground state.)

(b) Treating simultaneously the initial and final states of a transition implies foregoing the bonus of the Rydberg-Ritz principle, which permits us to deal with a smaller set of separate stationary states rather than with the larger set of transitions. Paying this price seems fair when the correlations of the two states are strongly coupled as they are also in the theory of line profiles; some compensation is provided, as we shall see, by the elimination of irrelevant variables.

II. WAVE MECHANICS OF A TRANSITION

We take as our starting point a joint Schrödinger equation for the initial and final states of an atomic transition. For definiteness and simplicity, we consider the transitions of an Ar atom from its ground state $|3p^6\,{}^1S)$ to a continuum or discrete state $|3p^5\Psi\,{}^1P)$, omitting reference to inner shells and regarding Ψ as a single-electron d state even though transitions to s states also occur. While many treatments of the same problem represent the state Ψ as a superposition of a complete set of eigenstates of a Hartree-Fock Hamiltonian and calculate the coefficients of that superposition, we shall study instead the radial wave function of Ψ. Dealing directly with a transition permits one to concentrate both his attention and his computational effort on the *differences* between the energies and the electron distributions of the two states, which alone are relevant to the transition. As anticipated in Sec. I, we regard this step as an important extension of the theory of atomic (and molecular) spectra.

The combination of the ket symbol of one of the states with a bra symbol for the other represents a transition operator. Thus the symbol $|3p^5\Psi\,{}^1P)$-$(3p^6\,{}^1S|$ represents the transition from the ground to the excited state. The difference of the formal Schrödinger equations forthe two states yields our basic equation:

$$H|3p^5\Psi\,{}^1P)(3p^6\,{}^1S| - |3p^5\Psi\,{}^1P)(3p^6\,{}^1S|H = [H, |3p^5\Psi\,{}^1P)(3p^6\,{}^1S|] = E|3p^5\Psi\,{}^1P)(3p^6\,{}^1S| , \tag{1}$$

where H is the Hamiltonian and E is the energy difference of the two states, i.e., the excitation energy. Equation (1) pertains to exact states, even though we have labeled them for simplicity by a single configuration symbol. In the following we shall replace the bra and ket state symbols in Eq. (1) by their position representations, that is, by wave functions, with successive approximations.

A. Ordinary Hartree-Fock approximation

At the outset we represent the ground state of Ar approximately by the single-determinant wave function $(3p^6\,{}^1S|\cdots\vec{r}_i'\cdots)$ corresponding to the $3p^6$ configuration, where $\vec{r}_i'$ represents the *position and spin* coordinates of the ith electron, with $i=1, 2, \ldots, N$, and $N=18$. The radial wave functions $\chi_{nl}(r)$ for various subshells, $1s, 2s, \ldots, 3p$, are assumed to have been calculated by the standard Hartree-Fock (HF) procedure. The excited-state wave function $(\cdots\vec{r}_i\cdots|3p^5\Psi\,{}^1P)$ is that linear combination of determinants with alternative distributions of magnetic quantum numbers which yields ${}^1P$ character with total magnetic quantum M. (In photoabsorption, the value of M depends on the light polarization; we set $M = 0$.) Its radial wave functions are the same as for the ground state except for $\psi(r)$, the radial part of Ψ, which remains to be determined by the Schrödinger equation (1). Substitution of this wave function into the usual equation

$$H(\cdots \vec{r}_i \cdots | 3p^5 \Psi\, ^1P) = (\cdots \vec{r}_i \cdots | 3p^5 \Psi\, ^1P)\mathcal{E} ,$$

where H is the nonrelativistic Hamiltonian without spin-orbit coupling, would lead one to the frozen-core, ^1P-restricted, HF equation for $\psi(r)$. We shall show, by contrast, that substitution of the same form of wave function into the seemingly equivalent Eq. (1) yields additional terms.

The reduction of a many-particle wave equation to a single-particle radial equation proceeds by integrating over the positions of all but one particle and by factoring out the angular dependence. In our case, the pair of functions

$$(\cdots \vec{r}_i \cdots | 3p^5 \Psi\, ^1P)(3p^6\, ^1S | \cdots \vec{r}_i{}' \cdots) \tag{2}$$

constitutes a transition matrix and the reduction amounts to extracting from it the single-particle matrix which we call, in Löwdin's language,[24] the first-order transition matrix. Orthogonality of Ψ to all other occupied orbitals simplifies the calculation and yields, on the right-hand side of Eq. (1),

$$N\left(\prod_{i=2}^{N} \int\int d\vec{r}_i\, d\vec{r}_i{}'\, \delta(\vec{r}_i - \vec{r}_i{}')\right)(\cdots \vec{r}_i \cdots | 3p^5 \Psi\, ^1P)(3p^6\, ^1S | \cdots \vec{r}_i{}' \cdots) = \psi(r_1)(2, \hat{r}_1 | w_{00}^{[01]} | 1, \hat{r}_1{}')\chi_{3p}(r_1') . \tag{3}$$

On the right-hand side of Eq. (3) we have represented the dependence on spin and direction variables through a matrix symbol defined by

$$(l, \hat{r} | w_{\pi q}^{[\kappa k]} | l', \hat{r}') = (-1)^{(1/2) - m_s'}(\tfrac{1}{2}m_s, \tfrac{1}{2} - m_s' | \tfrac{1}{2}\tfrac{1}{2}\kappa\pi) \sum_{mm'} Y_{lm}(\theta\phi)(-1)^{l'-m'} Y^*_{l'm'}(\theta'\phi')(lm, l'-m' | l\, l' kq); \tag{4}$$

this matrix constitutes a space-coordinate representation of the double-tensor operator developed by Judd,[25] to within a normalization factor -1. Analogous basis sets of operators have been used in spectroscopy since Racah's early work. The symbols in parentheses on the right-hand side Eq. (4) indicate Wigner coefficients. The operator w in Eq. (3) has $\kappa = 0$ and $k = 1$, indicating that the transition leaves the spin unchanged and has dipole orbital character, while $\pi = 0$ and $q = 0$ indicate no change of the z components of spin and orbital momenta. The first-order transition matrix (3) is indicated, in a notation akin to Löwdin's, by $(\vec{r}_1 | \Gamma | \vec{r}_1{}')$, and serves to calculate matrix elements of single-particle operators in a condensed form. Thus the dipole moment of our excitation is calculated from Eq. (3) in the form

$$\begin{aligned}(3p^6\, ^1S | \sum_i z_i | 3p^5 \Psi\, ^1P) &= \int\int d\vec{r}_1\, d\vec{r}_1{}'\, z_1 \delta(\vec{r}_1 - \vec{r}_1{}')(\vec{r}_1 | \Gamma | \vec{r}_1{}') \\ &= \int d\hat{r}_1 \cos\theta_1\, (2, \hat{r}_1 | w_{00}^{[01]} | 1, \hat{r}_1) \int_0^\infty dr_1\, \chi_{3p}(r_1) r_1 \psi(r_1) = (\tfrac{4}{3})^{1/2}(\chi_{3p} | r | \psi) ,\end{aligned} \tag{5}$$

where the $\int d\hat{r}_1$ includes a sum over spin, $\sum_{m_s}$.

On the left-hand side of Eq. (1), the electron-electron interaction terms complicate the reduction to a single-particle equation. There arise nonlocal potential terms which involve integrals over wave functions of a second electron and which are substantially the same as appear in Hartree-Fock equations.[26] We represent these terms in the form of reduced matrix elements, defined as

$$(l \| V^k(a, b; r) \| l') = (l \| C^{[k]} \| l')(l_a \| C^{[k]} \| l_b) \times \int_0^\infty d\bar{r}\, a(\bar{r}) b(\bar{r}) r_<^k / r_>^{k+1} , \tag{6}$$

where $C^{[k]}$ matrix elements are standard[27] and restrict the values of k by requiring $k + l' - l$ to be even, $r_< = \min(r, \bar{r})$, and $a(\bar{r})$ and $b(\bar{r})$ indicate two radial wave functions. (The $C^{[k]}$ matrix elements of odd degree k are anti-Hermitian according to their usual definition; therefore the matrix V^k is Hermitian only with the proviso that Hermitian conjugation implies the transposition of a and b.) We also utilize the symbol H_l^N for the HF radial Hamiltonian of an electron with orbital quantum number l in the field of the neutral (N-electron) ground-state Ar atom, given in atomic units by

$$\begin{aligned}H_l^N f_l(r) = &\left(-\frac{1}{2}\frac{d^2}{dr^2} - \frac{Z}{r} + \frac{1}{2}\frac{l(l+1)}{r^2} + \sum_{n'l'}^{3p} \frac{[l']^{1/2}}{[l]^{1/2}} 2(l \| V^0(\chi_{n'l'}, \chi_{n'l'}; r) \| l)\right) f_l(r) \\ &- \frac{1}{[l]} \sum_{n'l'}^{3p} \sum_k (-1)^k (l \| V^k(\chi_{n'l'} f_l; r) \| l')\chi_{n'l'}(r) ,\end{aligned} \tag{7}$$

where $[l]=2l+1$. (Recall that the very same operator also determines the occupied bound-state orbitals, $H_{l'}^{N}\chi_{n'l'}=\epsilon_{n'l'}\chi_{n'l'}$.) With these definitions and with the approximate representation (2) of the first-order transition matrix, Eq. (1) reduces to the radial equation

$$\left[\left(H_2^N-\epsilon_{3p}-E-\sum_k\begin{Bmatrix}2&2&k\\1&1&1\end{Bmatrix}(2\|V^k(\chi_{3p},\chi_{3p};r_1)\|2)\right)\psi(r_1)-\tfrac{2}{3}(2\|V^1(\chi_{3p},\psi;r_1)\|1)\chi_{3p}(r_1)\right](2,\hat{r}_1|w_{00}^{[01]}|1,\hat{r}_1')\chi_{3p}(r_1')$$
$$+\chi_{3p}(r_1)(1,\hat{r}_1|w_{00}^{[01]}|2,\hat{r}_1')\chi_{3p}(r_1')\sum_k\left(\tfrac{2}{3}\delta_{k1}-\begin{Bmatrix}2&1&k\\2&1&1\end{Bmatrix}\right)(1\|V^k(\chi_{3p},\psi;r_1')\|2)+\cdots=0\,,\qquad(8)$$

where the dots stand for terms corresponding to $3p\rightarrow s$ and to inner-shell excitations, which have been omitted for simplicity. In the large square brackets of Eq. (8), ϵ_{3p} originates from the application of H to $\chi_{3p}(r')$, the $\sum_k$ terms represent the attractive field exerted by the $3p$ vacancy upon the excited electron, and the last term, $\frac{2}{3}(2\|V^1\|1)$, represents the strong repulsion associated with excitation transfer among the $3p$ electrons, which is characteristic of collective excitations and which shifts their oscillator-strength distribution toward higher frequencies (Sec. 6.1 of Ref. 22). The terms in the large square brackets resulting from the presence of a $3p$ vacancy can be absorbed into the definition of a HF Hamiltonian H^{N-1} for an electron with $l=2$ moving in the field of a core with a $3p$ vacancy,

$$H_{(3p)2}^{N-1}f_2(r)=\left(H_2^N-\sum_k\begin{Bmatrix}2&2&k\\1&1&1\end{Bmatrix}\times(2\|V^k(\chi_{3p},\chi_{3p};r)\|2)\right)f_2(r)-\tfrac{2}{3}(2\|V^1(\chi_{3p},f_2;r)\|1)\chi_{3p}(r)\,,\qquad(9)$$

whereby the expression in the large square brackets of (8) reduces to

$$(H_{(3p)2}^{N-1}-\epsilon_{3p}-E)\psi(r_1)\,.\qquad(10)$$

The spin-angular matrix $w_{00}^{[01]}$ appears in the two groups of terms of Eq. (8) with alternative permutations of its indices (l,l'), namely, $(2,1)$ and $(1,2)$. This circumstance, essential for our problem, prevents immediate elimination of the spin and angular variables, that is, the reduction of Eq. (8) to a purely radial equation, and hence requires discussion.

The terms of Eq. (8) with the factor $(1,\hat{r}_1|w_{00}^{[01]}|2,\hat{r}_1')$ represent the exchange of k units ($k=1$ or 3) of orbital momentum between the excited and the $3p$ electrons, an action which is applied to the ground-state coordinate $\hat{r}_1'$. The invariance of the Hamiltonian under *joint* rotation of all electron coordinates permits all terms of Eq. (8) to depend on spin-angular matrices $w_{\pi q}^{[\kappa k]}$ with the same values of these indices; however, transfers of orbital momentum between electrons manifest themselves through the occurrence of different values of the indices (l,l'). Mathematically, the validity of any equation with the form $F(\hat{r},\hat{r}')=0$ for arbitrary $\hat{r}$ and $\hat{r}'$ implies that, upon expansion of F into a complete set of w matrices, the coefficient of *each term* vanishes. Hence Eq. (8) actually resolves into the two separate equations

$$(H_{(3p)2}^{N-1}-\epsilon_{3p}-E)\psi(r_1)=0\,,\qquad(11a)$$

$$\sum_{k=1,3}\left(\tfrac{2}{3}\delta_{k1}-\begin{Bmatrix}2&1&k\\2&1&1\end{Bmatrix}\right)(1\|V^k(\chi_{3p},\psi;r_1')\|2)=0,\quad(?)\,,\qquad(11b)$$

where the ? sign draws attention to their apparent inconsistency. Equation (11a) is a HF equation expressing the requirement that $(\cdots\vec{r}_i\cdots|3p^5\Psi\,{}^1P)$ be an approximate eigenfunction of H with the eigenvalue $\epsilon_{3p}+E$, but Eq. (11b) is generally incompatible with it. Thus we see that the usual HF equations for excited states disregard the electron-interaction effect represented by Eq. (11b). To take this effect into account, we are forced to generalize the simple trial form (2) of the transition matrix.

B. Ground-state correlations

The extension of the matrix (2) which we consider involves the introduction of correlations in the ground-state wave function $(\cdots\vec{r}_i\cdots|3p^6\,{}^1S)$, but only the very *minimum of correlations that is relevant* to the transition of interest. The possibility of minimizing this extension is afforded by our having restricted our goal to studying the transition between two states without any attempt at describing the separate states accurately. The appropriate minimal correlation consists of admixing in the ground-state wave function the virtual excitation of a pair of $3p$ electrons to d orbitals, whose radial wave functions, φ_a and φ_b, remain to be determined by solving the Schrödinger equation (1). Full determination of the admixture of this virtually excited state, $|3p^4\Phi_a\Phi_b\,{}^1S)$, with the unperturbed ground state $|3p^6\,{}^1S)$ would require the identification of its parentage and of the admixture coefficients. The parentage can be identified as a particular superposition of the three alternative couplings of $3p^4$ and of $(\Phi_a\Phi_b)$, namely, ${}^3P$, ${}^1D$, and ${}^1S$, with coefficients b_{SL}. The determination of these coefficients, of the normalization of φ_a and φ_b, and of the over-all normalization, will be considered later in the context of the solution of the Schrödinger equation.

We proceed then by replacing the initial trial form (2) of the transition matrix by

$$(\cdots \vec{\mathrm{r}}_i \cdots |3p^5\Psi\,{}^1P)[(3p^6\,{}^1S|\cdots \vec{\mathrm{r}}_i' \cdots) + (3p^4\Phi_a\Phi_b\,{}^1S|\cdots \vec{\mathrm{r}}_i' \cdots)]\,, \tag{12}$$

where the relative amplitude of the two terms is included in the normalization coefficients indicated above. Here and henceforth, the specification of the state in wave-function symbols such as $(3p^6\,{}^1S|\cdots \vec{\mathrm{r}}_i' \cdots)$ has its usual meaning of representing a Slater determinant or a linear superposition of determinants of a given configuration with the specified LS quantum numbers, whereas in Eq. (1) the symbol $(3p^6\,{}^1S|$ had been used for simplicity to indicate a ground state with an unspecified admixture of configurations. Our choice of virtual excitations to be admixed in the transition matrix (12) has the following main property: The first-order (i.e., single-particle) transition matrix to be derived from it includes, besides a term identical with Eq. (3), a second term whose spin-angular factor, $(1, \hat{r}_1|w_{00}^{[01]}|2, \hat{r}_1')$, coincides with that of the second group of terms of Eq. (8). The analytic expression of this matrix is

$$(\vec{\mathrm{r}}_1|\Gamma|\vec{\mathrm{r}}_1') = \psi(r_1)(2, \hat{r}_1|w_{00}^{[01]}|1, \hat{r}_1')\chi_{3p}(r_1') + \chi_{3p}(r_1)(1, \hat{r}_1|w_{00}^{[01]}|2, \hat{r}_1')\phi(r_1')\,, \tag{13}$$

where ϕ is a superposition of φ_a and φ_b,

$$\phi(r) = A_1[(\psi|\varphi_b)\varphi_a(r) + (\psi|\varphi_a)\varphi_b(r)]\,, \tag{14}$$

with

$$(\psi|\varphi_b) = \int_0^\infty \psi(r)\varphi_b(r)\,dr, \qquad A_k = \sum_{SL}(-1)^L \begin{Bmatrix} 2 & 2 & L \\ 1 & 1 & k \end{Bmatrix} b_{SL}\,. \tag{15}$$

Note that the matrix Γ depends on the parentage coefficients b_{SL} and on the radial functions φ_a and φ_b only through the single function $\phi(r)$. The analog of the dipole matrix element (5), calculated from the transition matrices (12) or (13), consists now of the sum of two terms

$$(\tfrac{4}{3})^{1/2}[(\chi_{3p}|r|\psi) - (\phi|r|\chi_{3p})]\,. \tag{16}$$

The minus sign in this equation derives from the angular integration; the ket and bra positions of ψ and ϕ in the matrix elements correspond to those in Eq. (12). The introduction of the second term in Eq. (16) is characteristic of many-body theories.

The construction of the first-order matrix, Eq. (13), and of the single-particle equation, which results by substituting Eq. (12) into Eq. (1) and integrating over $\vec{\mathrm{r}}_2, \ldots, \vec{\mathrm{r}}_N$ as in Eq. (3), constitutes a straightforward but lengthy task. Indeed, Eq. (12) represents the superposition of a large number of products of Slater determinants, and the calculation of electron interactions involves extensive applications of angular-momentum algebra. To perform this task in a condensed form, keeping in sight the tensorial properties of the transition matrices, we have developed an application of Racah techniques to transition matrices and to the reductions of their Schrödinger equation. This development is reported in a companion paper[28] and we give here only the results.

The Schrödinger equation (1) for the transition matrix (12) reduces to a linear combination of spin-angular density matrices whose structure we indicate as

$$\{\cdots\}(2, \hat{r}_1|w_{00}^{[01]}|1, \hat{r}_1') + \{\cdots\}(1, \hat{r}_1|w_{00}^{[01]}|2, \hat{r}_1') + \cdots = 0\,. \tag{17}$$

Here, as in Eq. (8), the last set of dots represents additional terms involving spin-angular matrices with (l, l') indices other than (2, 1) or (1, 2) and/or with radial wave functions of inner-shell electrons. These terms arise from $3p \rightarrow s$ transitions or from excitations of inner shells, which we omit here for simplicity and which are actually unimportant for many practical purposes. The dots in the two pairs of curly brackets in Eq. (17) represent two expressions which depend only on the radial coordinates r_1 and r_1'; *each* of these expressions must be set to zero in order that Eq. (17) be satisfied for all $(\hat{r}_1, \hat{r}_1')$.

The first expression yields

$$\left[(H^{N-1}_{(3p)2}-\epsilon_{3p}-E)\psi(r_1)-\sum_k\left(\tfrac{2}{3}\delta_{k1}-\begin{Bmatrix}2&1&k\\2&1&1\end{Bmatrix}-\frac{A_k}{5A_1}\right)(2\|V^k(\phi,\chi_{3p};r_1)\|1)\chi_{3p}(r_1)\right]\chi_{3p}(r_1')$$

$$-\tfrac{1}{3}\psi(r_1)\sum_k A_k[\varphi_a(r_1')(2\|V^k(\chi_{3p},\varphi_b;r_1')\|1)+\varphi_b(r'_1)(2\|V^k(\chi_{3p},\varphi_a;r_1')\|1)]=0\ , \quad (18)$$

with the notations of Eqs. (14) and (15). Equation (18) is not yet in final form because it cannot be reduced to an equation in r_1 alone by factoring out the radial function $\chi_{3p}(r_1')$, as we had done in Eq. (8). This circumstance suggests that our trial matrix (12) is still not sufficiently general, but we postpone a discussion of this hint until Sec. IV and proceed here to eliminate the dependence of Eq. (18) on r_1' by projecting it on $\chi_{3p}(r_1')$, i.e., by multiplying it with $\chi_{3p}(r_1')$ and integrating over r_1'. This operation eliminates $\chi_{3p}(r_1')$ from the first line of Eq. (18) and reduces the expression in the square brackets in the second line to a matrix element of the Coulomb interaction, thus bringing Eq. (18) to the form

$$[H^{N-1}_{(3p)2}-\epsilon_{3p}-E]\psi(r_1)-\sum_k\left[\tfrac{2}{3}\delta_{k1}-\begin{Bmatrix}2&1&k\\2&1&1\end{Bmatrix}\right](2\|V^k(\phi,\chi_{3p};r_1)\|1)\chi_{3p}(r_1)$$

$$+\sum_k\frac{A_k}{5A_1}(2\|V^k(\phi,\chi_{3p};r_1\|1)\chi_{3p}(r_1)-\tfrac{2}{3}\psi(r_1)\sum_k A_k(\varphi_a\chi_{3p}\|V^k\|\chi_{3p}\varphi_b)=0\ , \quad (19a)$$

where

$$(ab\|V^k\|cd)=\int_0^\infty dr\,a(r)(l_a\|V^k(b,d;r)\|l_c)c(r)\ .$$

Setting to zero the expression in the second curly brackets of Eq. (17) and applying a procedure analogous to that which reduced Eq. (18) to Eq. (19a) yields the equation for $\phi(r_1')$:

$$\left[H^{N-1}_{(3p)2}-\epsilon_{3p}+E)\phi(r_1')-\chi_{3p}(r_1')\sum_k\left(\tfrac{2}{3}\delta_{k1}-\begin{Bmatrix}2&1&k\\2&1&1\end{Bmatrix}\right)(1\|V^k(\chi_{3p},\psi;r_1'\|2)\right]$$

$$-\frac{1}{A_1}\sum_k\left(A_k\begin{Bmatrix}2&1&k\\2&1&1\end{Bmatrix}\chi_{3p}(r_1')(1\|V^k(\chi_{3p},\phi;r_1')\|2)\right.$$

$$\left.-\phi(r_1')[B_k(1,2)(2\|V^k(\chi_{3p},\chi_{3p};r_1')\|2)-C_k(1,2)(\chi_{3p}\chi_{3p}\|V^k\|\chi_{3p}\chi_{3p})]\right)$$

$$+\sum_k\left(A_k\begin{Bmatrix}2&1&k\\2&1&1\end{Bmatrix}[\varphi_a(r_1')(\chi_{3p}\varphi_b\|V^k\|\psi\chi_{3p})+\varphi_b(r_1')(\chi_{3p}\varphi_a\|V^k\|\psi\chi_{3p})]\right.$$

$$+B_k(2,1)[\varphi_a(r_1')(\chi_{3p}\varphi_b\|V^k\|\chi_{3p}\psi)+\varphi_b(r_1')(\chi_{3p}\varphi_a\|V^k\|\chi_{3p}\psi)]$$

$$\left.+C_k(2,1)[\varphi_a(r_1')(2\|V^k(\psi,\varphi_b;r_1')\|2)+\varphi_b(r_1')(2\|V^k(\psi,\varphi_a;r_1')2)]\right)=0\ , \quad (19b)$$

where

$$B_k(l,l')=-\sum_{SL}\begin{Bmatrix}l&k&l\\1&l'&l\\l'&l'&L\end{Bmatrix}b_{SL}\ ,\qquad C_k(l,l')=\sum_{SL}\begin{Bmatrix}l&l&L\\l&l&k\end{Bmatrix}\begin{Bmatrix}l&l&L\\l'&l'&1\end{Bmatrix}b_{SL}\ . \quad (20)$$

The expressions indicated by the last set of dots of Eq. (17) yield additional terms and equations having the same structure as Eqs. (19) but with other values of quantum numbers and different radial functions; the complete expressions are given in Appendix A.

We introduce the discussion of the rather complicated pair of Eqs. (19) by selecting out of them those terms which will be identified with the RPA approximation in Sec. III A,

$$(H^{N-1}_{(3p)2} - \epsilon_{3p} - E)\psi(r_1) - \sum_k \left(\tfrac{2}{3}\delta_{k1} - \begin{Bmatrix} 2 & 1 & k \\ 2 & 1 & 1 \end{Bmatrix}\right)(2\| V^k(\phi, \chi_{3p}; r_1)\|1)\chi_{3p}(r_1) \simeq 0 \,, \tag{21a}$$

$$(H^{N-1}_{(3p)2} - \epsilon_{3p} + E)\phi(r_1') - \sum_k \left(\tfrac{2}{3}\delta_{k1} - \begin{Bmatrix} 2 & 1 & k \\ 2 & 1 & 1 \end{Bmatrix}\right)(2\| V^k(\psi, \chi_{3p}; r_1')\|1)\chi_{3p}(r_1') \simeq 0 \,, \tag{21b}$$

where the last term has been rewritten to emphasize the symmetry of the two equations. The structure of this pair of equations is made apparent by considering Eq. (8) once again. That equation consists of two terms with different spin-orbit factors: The first of them contains in large square brackets expression $(H^{N-1}_{(3p)2} - \epsilon_{3p} - E)\psi(r)$ which now appears in Eq. (21a), while the essential part of the second term constitutes now the second term of Eq. (21b). Recalling also that Eq. (8), originating as the Schrödinger equation for the single-term transition matrix (2), resolves into the pair of inconsistent equations (11), we see that the introduction of the two-term transition matrix appears to have had the effect of complementing Eqs. (11) so as to make them consistent in this particular respect. The complement involves the additional wave function $\phi(r_1')$, whereby the pair of equations (21) constitutes a system of coupled HF equations. The extensive agreement with experiment achieved by RPA calculations[2] equivalent to the solution of this system indicates low importance of the terms which we have initially left aside from the complete equations (19) but proceed now to discuss.

To this end we outline part of the derivation of Eqs. (19) from the general Eq. (1). Since the Hamiltonian,

$$H = \sum_i H_0(\vec{r}_i) + \tfrac{1}{2} \sum_{i \neq j} V(\vec{r}_i - \vec{r}_j) \,, \tag{22}$$

consists of single- and two-particle terms, the process of integrating over all electron coordinates but $(\vec{r}_1, \vec{r}_1')$, as in Eq. (3), is nontrivial for the next-to-the-last pair, $(\vec{r}_2, \vec{r}_2')$. This point has been covered explicitly in textbooks (e.g., p. 16 of Ref. 9) for the case of density matrices such as

$$(\cdots \vec{r}_i \cdots | 3p^6\,{}^1S)(3p^6\,{}^1S| \cdots \vec{r}_i' \cdots)$$

consisting of two identical wave functions, but our case of transition matrices consisting of two different wave functions is equivalent in this respect. After $(N-1)$-fold integration, the Schrödinger equation (1) has the general form

$$H_0(r_1)(\vec{r}_1|\Gamma|\vec{r}_1') - (\vec{r}_1|\Gamma|\vec{r}_1')H_0(r_1') + \int\int d\vec{r}_2\, d\vec{r}_2' [V(\vec{r}_1 - \vec{r}_2) - V(\vec{r}_1' - \vec{r}_2')](\vec{r}_1, \vec{r}_2|\Gamma|\vec{r}_1', \vec{r}_2')\delta(\vec{r}_2 - \vec{r}_2') = E(\vec{r}_1|\Gamma|\vec{r}_1') \,, \tag{23}$$

which involves not only the first-order but also the second-order transition matrix. Our N-particle matrix, Eq. (12), yields the first-order matrix (13) and, as shown in a companion paper,[28] the second-order matrix

$$\begin{aligned}
(\vec{r}_1, \vec{r}_2|\Gamma|\vec{r}_1', \vec{r}_2') = {} & \tfrac{1}{2}(1 - P_{12})(1 - P_{1'2'}) \\
& \times \Bigg[(\vec{r}_1|\Gamma|\vec{r}_1') \sum_{nl}^{3p} (2[l])^{1/2} \chi_{nl}(r_2)(l, \hat{r}_2| w^{[00]}_{00} | l, \hat{r}_2')\chi_{nl}(r_2') \\
& - \sum_{\kappa k k'} \frac{(-1)^k}{A_1} \left(\frac{[k]}{2}\right)^{1/2} \begin{Bmatrix} k' & 1 & k \\ 1 & 1 & 2 \end{Bmatrix} c_{\kappa k'} \chi_{3p}(r_1)\chi_{3p}(r_2) \\
& \quad \times [(1, \hat{r}_1| w^{[\kappa k]} | 1, \hat{r}_1')(1, \hat{r}_2| w^{[\kappa k']} | 2, \hat{r}_2')]^{[01]}_{00} \chi_{3p}(r_1')\phi(r_2') \\
& - \sum_{\kappa k k'} (-1)^{k'} \left(\frac{[k]}{2}\right)^{1/2} \begin{Bmatrix} k' & 1 & k \\ 2 & 2 & 1 \end{Bmatrix} c_{\kappa k'} \psi(r_1)\chi_{3p}(r_2) \\
& \quad \times [(2, \hat{r}_1| w^{[\kappa k]} | 2, \hat{r}_1')(1, \hat{r}_2| w^{[\kappa k']} | 2, \hat{r}_2')]^{[01]}_{00} [\varphi_a(r_1')\varphi_b(r_2') + \varphi_b(r_1')\varphi_a(r_2')] \Bigg] \,,
\end{aligned} \tag{24}$$

where P_{12} and $P_{1'2'}$ are the operators that permute $(\vec{r}_1, \vec{r}_2)$ and $(\vec{r}_1', \vec{r}_2')$, respectively, and

$$c_{\kappa k'} = \sum_{SL} (-1)^{\kappa + k'}([\kappa][k'])^{1/2} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ \frac{1}{2} & \frac{1}{2} & \kappa \end{Bmatrix} \begin{Bmatrix} 2 & 2 & L \\ 1 & 1 & k' \end{Bmatrix} b_{SL} \,.$$

The first term in the large square brackets of Eq. (24) is the product of our first-order transition matrix and of the first-order density matrix of the ground state $|3p^6\,{}^1S)$.[28] The RPA equations (21) result if *only this first term* is retained in Eq. (23). The second term in the large square brackets of Eq. (24) depends, like the first term, on the wave function $\phi(r')$ rather than on the separate wave functions φ_a and φ_b. Its contribution to Eqs. (19) can be identified as the second group of terms in both equations. One might then conceive of adding this second group of terms to those retained in the RPA equations (21) without apparently spoiling the property of forming a system of two coupled equations for the wave functions ψ and ϕ. Note, however, that this additional group of terms depends on combinations of the parentage coefficients b_{SL} different from their combination A_1 which is included as a coefficient of ϕ itself. The last term in the large square brackets of Eq. (24) yields the last group of terms in both Eqs. (19). These terms depend, in contrast to those discussed above, on the separate functions φ_a and φ_b through their correlated product $\varphi_a(r_1')\varphi_b(r_2') + \varphi_b(r_1')\varphi_a(r_2')$. Thus we see that Eqs. (19) involve unknown functions other than the pair (ψ, ϕ) and are accordingly insufficient to determine them all. To proceed, one must either disregard the additional functions or introduce additional relations. We return to this matter in Sec. IV.

Retention by the RPA of only the first term in the large square brackets of Eq. (24) may be rationalized by remarking that only this term includes contributions by the full $3p^6$ shell of Ar. This is shown by noticing that the integral

$$\int\int d\vec{r}_2\, d\vec{r}_2'\, \delta(\vec{r}_2 - \vec{r}_2')(2[1])^{1/2}\chi_{3p}(r_2) \times (1, \hat{r}_2 | w_{00}^{[00]} | 1, \hat{r}_2')\chi_{3p}(r_2') = 6$$

represents the number of electrons of that shell. The contributions of the other terms of the transition matrix (24) to Eqs. (19) might then be expected to be small by virtue of including factors of the order of $\frac{1}{6}$. However, this expectation is not readily verified by closer inspection of the equations. A detailed evaluation of the various terms of Eqs. (19) exceeds the scope of this paper, but each term is interpreted by inspection as a particular element of the interaction among particles and holes, keeping in mind the restrictions upon the values of k arising from parity selection rules. For example, the terms with the coefficients B_k represent interactions between a particle and a vacancy, while those with C_k represent interactions between two particles or two holes.

We come now to consider the normalization of our wave functions. As noted above, it is an important feature of many-body theories that they deal with the evaluation of transition amplitudes, or transition matrices, rather than with the separate evaluation of wave functions for the initial and final states (see, e.g., p. 57 of Ref. 9). Accordingly, even their normalizations should not be carried out separately. Consider, e.g., what would happen by applying the usual procedure for orthonormalizing the set of wave functions ψ with different excitation energies E. This procedure considers pairs of solutions $(\psi, \bar{\psi})$ of the relevant wave equation—Eq. (19a) or (21a) in our case—for a pair of excitation energies $(E, \bar{E})$. From the equations, one forms the expression $(\bar{E} - E)(\psi|\bar{\psi}) - [(\psi|H|\bar{\psi}) - (\bar{\psi}|H|\psi)] = 0$; in the usual procedure, the term in square brackets reduces to an integral over a surface of very large radius, by application of Green's theorem. In our case, however, this procedure would fail because the coupling terms including the wave function ϕ do not cancel out in the square brackets.

We are thus led to perform a simultaneous orthonormalization of the pair of wave functions $\psi(r)$ and $\phi(r)$ by manipulation of the *whole system* of RPA equations (21). More specifically, we consider the RPA equations (21) for two different excitation energies E and $\bar{E}$, with alternative solutions (ψ, ϕ) and $(\bar{\psi}, \bar{\phi})$. The equations with energy E are multiplied by $\bar{\psi}$ and $\bar{\phi}$, respectively, integrated over r_1 (or r_1') and summed; the two equations with energy $\bar{E}$ are handled in the corresponding way. Upon subtraction of the expressions thus obtained for E and $\bar{E}$, the coupling terms do cancel and we obtain

$$\lim_{R\to\infty} \left((\bar{E} - E) \int_0^R dr\, [\bar{\psi}(r)\psi(r) - \bar{\phi}(r)\phi(r)] + (\text{surface terms at } r = R) \right) = 0 \,. \quad (25)$$

This equation requires the radial integral to vanish when $\bar{E}$ is an eigenvalue not equal to E, because the surface terms then yield no contribution.[29] In the limit $\bar{E} \to E$, on the other hand, the ratio of the surface terms to $\bar{E} - E$ yields the value of the radial integral, and hence the normalization constant, in terms of the asymptotic expression of $\psi(R)$. [The wave function $\phi(R)$ does not contribute to the surface terms because it vanishes much faster than $\psi(R)$ as $R\to\infty$, even in the discrete spectrum, owing to the sign of E in Eq. (21b).] The quantity to be normalized is thus the limit, for $\overline{E}\to E$, of the integral of $\overline{\psi}\psi-\overline{\phi}\phi$, which will be identified in Sec. III A with the corresponding expression of the RPA treatment. We also note that this normalization procedure complements Eqs. (21) to the extent of determining the absolute magnitudes besides the r dependence of $\psi(r)$ and $\phi(r)$, but fails to determine any of the additional parameters of the virtual excitation which have remained unspecified in Eq. (12).

The cancellation of coupling terms of Eqs. (21), which has led to the orthonormalization formula (25), no longer occurs when the same procedure is applied to Eqs. (19). This observation confirms that the non-RPA terms of Eqs. (19) should not be regarded simply as a correction to be added to the RPA equations (21). They indicate that a consistent treatment, more accurate than the RPA, hinges on the use of a more accurate form of the transition matrix than is provided by Eq. (12), and on the formulation and solution of an equation for the second-order matrix analogous to Eq. (23).

III. INTERCONNECTIONS

A. The RPA method

The RPA method considers a single-particle (i.e., first-order) transition operator in the second quantization representation, with the form[8]

$$Q^{\dagger}=X_{ni}a_{n}^{\dagger}a_{i}-Y_{in}a_{i}^{\dagger}a_{n}\ , \tag{26}$$

where the pair of creation-annihilation operators $a_n^{\dagger}a_i$ shifts one particle from a spin orbital i to a spin orbital n. Each of these spin orbitals is identified by spin and orbital quantum numbers m_s, l, m, and by the energy eigenvalue of a radial eigenfunction of the HF Hamiltonian H_l^N defined by Eq. (7). Indices i (or j) pertain to orbitals which are occupied in the ground state of the system, indices n (or m) to excited states; the treatment of Ar in Sec. II implies restricting (i,j) to $3p$ and (n,m) to d orbitals. Allowing for the difference of representation, the operator (26) is seen to be equivalent to the transition matrix (13), with the coefficients X_{ni} and Y_{in} playing the same role as the radial wave functions $\psi(r)$ and $\phi(r)$, respectively. Both pairs have to be determined by solving a Schrödinger equation; Sec. II has reduced Eq. (1) to Eqs. (19); here, we start from

$$[H,Q^{\dagger}]=EQ^{\dagger}\ . \tag{27}$$

[RPA treatments do not usually assign a specific multipolarity to the operator $Q^{\dagger}$ at the outset, whereas we have been dealing in Sec. II explicitly with a dipole operator. However it emerges later, e.g., in Sec. 2.3 of Ref. 2, that Eq. (27) resolves into separate equations for operators $Q^{\dagger}$ of different multipolarity.]

In the second quantization representation, the Hamiltonian takes the form

$$H=\sum_{\alpha\beta}(\alpha|H_0|\beta)a_{\alpha}^{\dagger}a_{\beta}+\sum_{\alpha\beta\gamma\delta}(\alpha\beta|V|\gamma\delta)a_{\alpha}^{\dagger}a_{\beta}^{\dagger}a_{\delta}a_{\gamma}\ , \tag{28}$$

which consists of single and two-particle terms, the latter arising from electron-electron interactions. Greek letters denote either (i,j) or (m,n) indices. The commutator of a single- (two-) particle operator with the operator $Q^{\dagger}$ of Eq. (26) yields again a single- (two-) particle operator. Consequently the complete Eq. (27) includes single- and two-particle operator terms. This result is the counterpart of the fact, noted in Sec. II B, that Eq. (23) interrelates first- and second-order transition matrices.

The RPA proceeds at this point to reduce Eq. (27) to a single-particle form through a two-step *linearization approximation*: (i) It retains only those two-particle terms of Eq. (27) whose operators $a_{\alpha}^{\dagger}a_{\beta}^{\dagger}a_{\delta}a_{\gamma}$ have just one index of the (m,n), i.e., "excited-orbital" type. This approximation is made plausible, in applications to atoms or nuclei, on the grounds that the operators with two or more (m,n) indices represent interactions between pairs of excited particles, and that such double excitations are less likely than single excitations; similarly, the terms with no (m,n) indices would represent interactions between vacancies. In the original applications of RPA to very large systems it was argued that terms of Eq. (27) that are due to interactions between many alternative pairs of excited particles tend to cancel out because their coefficients have quite different ("random") phases. (ii) It replaces pairs of unexcited particle operators $a_i^{\dagger}a_j$ by their ground-state average value δ_{ij}.

These simplifications reduce Eq. (27) to the form

$$\sum_{ni}\left((\epsilon_n-\epsilon_i-E)X_{ni}+\sum_{mj}(nj|\tilde{V}|im)X_{mj}+\sum_{mj}(nm|\tilde{V}|ij)Y_{jm}\right)a_n^{\dagger}a_i$$
$$+\sum_{ni}\left((\epsilon_n-\epsilon_i+E)Y_{in}+\sum_{mj}(im|\tilde{V}|nj)Y_{jm}+\sum_{mj}(ij|\tilde{V}|nm)X_{mj}\right)a_i^{\dagger}a_n=0\ , \tag{29}$$

where $(\alpha\beta|\tilde{V}|\gamma\delta) = (\alpha\beta|V|\gamma\delta) - (\alpha\beta|V|\delta\gamma)$. The basic system of linear equations of the RPA emerges now by equating to zero the two expressions in the large parentheses of Eq. (29), i.e., the coefficients of the two operators $a_n^\dagger a_i$ and $a_i^\dagger a_n$; this step is wholly analogous to our having set to zero the coefficients of the two spin-angular matrices of Eq. (17). (A procedure for solving the resulting infinite system of coupled equations is outlined in Appendix B.) The term $\sum_{mj}(nj|\tilde{V}|im)X_{mj}$ in the first large parentheses of Eq. (29) and the term $\sum_{mj}(im|\tilde{V}|nj)Y_{jm}$ in the second large parentheses are equivalent to the terms of Eq. (9) which were combined with the Hamiltonian H^N to yield $H^{N-1}_{(3p)2}$, if i and j are restricted to $3p$ orbitals as we have done in Sec. II; this term can then be deleted with the understanding that the index n will apply henceforth to eigenstates of $H^{N-1}_{(3p)2}$ rather than of H^N. [Amusia *et al.* perform the same transformation (see, e.g., Sec. 2.4 of Ref. 2); however, in their notation, the index $N+1$ replaces our N. Their analytical treatment also retains the terms with $j \neq 3p$ to allow for transfer of excitation from one shell to another, whereas we are disregarding such transfers for simplicity.]

The RPA equations thus obtained from Eq. (29),

$$\begin{aligned}(\epsilon_n - \epsilon_i - E)X_{ni} + \sum_{mj}(nm|\tilde{V}|ij)Y_{jm} = 0\ ,\\ (\epsilon_n - \epsilon_i + E)Y_{in} + \sum_{mj}(ij|\tilde{V}|nm)X_{mj} = 0\ ,\end{aligned} \tag{30}$$

are equivalent to Eqs. (21) of Sec. II B. The equivalence is demonstrated in two steps. The first step consists of factoring out of Eq. (30) the dependence on all spin and magnetic quantum numbers which is included in the indices m, n, i, and j, and is represented by 3-j coefficients. This operation amounts to reducing Eqs. (30), regarded as representations of the group of space rotations, and is included in the calculations performed by Amusia *et al.* (e.g., in Sec. 2.3 of Ref. 2). It brings the matrix elements of $\tilde{V}$ to the form of reduced matrix elements which, together with the coefficients X_{ni} and Y_{in}, depend now only on the eigenvalues ϵ_n. In the second step, one multiplies each Eq. (30) by the eigenfunction $\psi_n(r)$ of $H^{N-1}_{(3p)2}$ corresponding to the eigenvalue ϵ_n and sums over all n, of both the discrete and continuum. Substituting in Eqs. (30)

$$\begin{aligned}&\epsilon_n\psi_n = H^{N-1}_{(3p)2}\psi_n\ ,\\ &\sum_n \psi_n(r)X_{ni} = \psi(r),\quad \sum_n Y_{in}\psi_n(r) = \phi(r)\ ,\end{aligned} \tag{31}$$

and using the completeness relation

$$\sum_n \psi_n(r)\psi_n(r') = \delta(r - r') \tag{32}$$

to transform the matrix elements of $\tilde{V}$ into potential terms completes the demonstration.

A correspondence between the terms of $[H, Q^\dagger]$ discarded in the linearization process and the non-RPA terms of Eqs. (19) emerges from the following considerations: Within the framework of the present paper, which considers only transitions between $3p$ and d orbitals, parity conservation yields only two-particle terms of $[H, Q^\dagger]$ that include either (a) three creation or annihilation operators of the $3p$ shell (i,j) and one of the d orbitals (m,n), or (b) one (i,j) and three (m,n) operators. Step (ii) of the linearization approximation acts on the terms of type (a) by replacing one operator pair $a_i^\dagger a_j$ by δ_{ij}; the terms thus disregarded correspond to those retained in the second group of terms of Eq. (24), which involves the single excited orbital $\phi(r_1')$. Step (i) of the linearization discards instead the terms of type (b), with three excited orbital operators, and thus corresponds to discarding the third group of terms of Eq. (24), which contains all three orbitals ψ, φ_a, and φ_b.

B. Time-dependent Hartree-Fock method

This method studies small oscillatory departures of the state of a system from a ground state represented by a single-determinant wave function. In our example of Ar, the ground-state wave function takes the form

$$(\cdots \vec{r}_i \cdots;t|\Phi_0) = N!^{-1/2}\,\mathrm{Det}|\chi_\alpha(\vec{r}_i)|\exp(-iE_0t/\hbar),\quad (\alpha, i) = 1, \ldots, 18\ , \tag{33}$$

where the index α labels the 18 occupied spin orbitals. Unspecified oscillations of this state are represented by adding to each spin orbital χ_α an increment proportional to a small parameter $\lambda\exp(\pm i\omega t)$—and orthogonal to all χ_α—as indicated by the substitution

$$\chi_\alpha(\vec{r}_i) \rightarrow \chi_\alpha(\vec{r}_i) + \lambda\phi_\alpha(\vec{r}_i)e^{i\omega t} + \lambda\psi_\alpha(\vec{r}_i)e^{-i\omega t}\ , \tag{34}$$

which implies

$$\Phi_0 \rightarrow \Phi = \Phi_0 + \lambda\Phi_1 + \lambda^2\Phi_2 + \cdots\ . \tag{35}$$

(The notation is designed here to facilitate comparisons with Sec. II.) Hartree-Fock equations for the orbitals χ_α, ϕ_α, and ψ_α are obtained by entering the wave function Φ in the variational expression

$$\delta(\Phi|H - i\hbar\partial/\partial t|\Phi) = 0\ , \tag{36}$$

applying the variation in turn to each of the orbitals and keeping terms to first order in λ only. The Hamiltonian may include an external potential term which drives the oscillations of Φ; in our example this term might take the form $\lambda F \sum_i e z_i \cos\omega t$, where λF represents the peak strength of an electric field and z_i a cartesian coordinate of the ith electron.

The terms of Eq. (36) that are of zeroth order in λ lead to the usual HF equations for the spin orbitals χ_α. The first-order terms lead to coupled equations for the ϕ_α and ψ_α which have the general structure of those of Sec. II and are actually equivalent to the RPA equations of Sec. III A, as detailed further below. Indeed, both the initial application of RPA in nuclear physics[9] and the most recent review of atomic applications[2] have followed the route starting from the TDHF formulation. To compare the TDHF approach with that of Sec. II and to identify the role of time dependence, we shall utilize the fact that all the equations for radial wave functions considered in this paper may be regarded as obtained from the Schrödinger equation (23) in terms of first- and second-order Γ matrices, by elimination of spin-angular factors and of one set of radial functions. Alternative approaches correspond to the use of different approximations for the Γ matrices. The presence of the $\partial/\partial t$ operator in Eq. (36) does not disturb us, as long as all time-dependent factors are exponential.

The construction of Γ matrices from TDHF wave functions is facilitated by the fact that the N-particle density matrix corresponding to a single-determinant wave function is obtained by matrix multiplication in the form of a single determinant. Thus Eq. (33) leads to

$$(\cdots \vec{r}_i \cdots ; t|\Phi_0)(\Phi_0|\cdots \vec{r}_j^{\,\prime} \cdots ; t) = N!^{-1}\,\mathrm{Det}\left|\sum_\alpha \chi_\alpha(\vec{r}_i)\chi_\alpha(\vec{r}_j^{\,\prime})\right| . \tag{37}$$

Substitution of Φ for Φ_0 in this equation is equivalent to the substitution of Eq. (34) on its right-hand side. Subsequent integration over $i > 1$ according to Eq. (3) leads then [see, e.g., Eq. (2.20) of Ref. 9] to the first-order matrix

$$\begin{aligned}(\vec{r}_1|\Gamma(t)|\vec{r}_1^{\,\prime}) = \sum_\alpha \{ &\chi_\alpha(\vec{r}_1)\chi_\alpha^*(\vec{r}_1^{\,\prime}) + \lambda[\psi_\alpha(\vec{r}_1)\chi_\alpha^*(\vec{r}_1^{\,\prime}) + \chi_\alpha(\vec{r}_1)\phi_\alpha^*(\vec{r}_1^{\,\prime})]e^{-i\omega t}\\ &+\lambda[\phi_\alpha(\vec{r}_1)\chi_\alpha^*(\vec{r}_1^{\,\prime}) + \chi_\alpha(\vec{r}_1)\psi_\alpha^*(\vec{r}_1^{\,\prime})]e^{i\omega t} + O(\lambda^2)\} .\end{aligned} \tag{38}$$

According to usual conventions, the terms of this matrix with time dependence $\exp(\mp i\omega t)$ represent, respectively, the conjugate transition matrices pertaining to absorption or emission by the atom of a quantum $\hbar\omega$. Accordingly, the wave functions $\psi_\alpha(r_i)$ represent excited single-particle states that can be actually reached in an absorption process, while the ϕ_α, which appear in Eq. (34) with the opposite factor $\exp(i\omega t)$, correspond to virtual excitations. Indeed, the term

$$\sum_\alpha [\psi_\alpha(\vec{r}_1)\chi_\alpha^*(\vec{r}_1^{\,\prime}) + \chi_\alpha(\vec{r}_1)\phi_\alpha^*(\vec{r}_1^{\,\prime})]$$

of Eq. (38) can be made to coincide with the matrix for an excitation transition, Eq. (13), by restricting the $\sum_\alpha$ to $3p$ orbitals and the ψ_α and ϕ_α to d orbitals, as we have done for simplicity in Sec. II.

Two remarks can already be made at this point. The introduction of time dependence in the variational expression (36) has served to sort out the terms of the first-order matrix that correspond to absorption or emission processes, and particularly to combine in each of them contributions that originate from different terms of Eq. (34) and correspond to real or virtual transitions, respectively. Secondly, a single wave function ϕ represents the contribution of virtual excitations of the ground state to both first-order matrices, Eqs. (13) and (38), even though such excitations must involve a pair of particles in any HF model. The excitation of a pair was displayed explicitly in Sec. II and projected into a single wave function by Eq. (14), whereas it is only implied in the TDHF procedures (except as manifested in diagrammatic representations).

The difference between the TDHF approach and that of Sec. II emerges as we proceed to compare second-order matrices. Substitution of Φ for Φ_0 in Eq. (37) and integration over $i > 2$ leads [see, e.g., Eq. (2.24) of Ref. 9] to

$$\begin{aligned}(\vec{r}_1,\vec{r}_2|\Gamma(t)|\vec{r}_1^{\,\prime},\vec{r}_2^{\,\prime}) = {}&\tfrac{1}{2}(1-P_{1'2'})\sum_\alpha \chi_\alpha(\vec{r}_1)\chi_\alpha^*(\vec{r}_1^{\,\prime})\sum_\beta \chi_\beta(\vec{r}_2)\chi_\beta^*(\vec{r}_2^{\,\prime})\\ &+\tfrac{1}{2}\lambda(1-P_{12})(1-P_{1'2'})\sum_\alpha \chi_\alpha(\vec{r}_1)\chi_\alpha^*(\vec{r}_1^{\,\prime})\sum_\beta\{\psi_\beta(\vec{r}_2)\chi_\beta^*(\vec{r}_2^{\,\prime}) + \chi_\beta(\vec{r}_2)\phi_\beta^*(\vec{r}_2^{\,\prime})]e^{-i\omega t}\\ &+[\phi_\beta(\vec{r}_2)\chi_\beta^*(\vec{r}_2^{\,\prime}) + \chi_\beta(\vec{r}_2^{\,\prime})\psi_\beta^*(\vec{r}_2^{\,\prime})]e^{+i\omega t}\} + O(\lambda^2) ,\end{aligned} \tag{39}$$

where P_{12} and $P_{1'2'}$ indicate permutation operators as in Eq. (24). The term of this TDHF matrix of first order in λ and with the $\exp(-i\omega t)$ factor, which is relevant for comparison with Sec. II, corresponds to the first term only within the large square brackets of Eq. (24). The additional terms of Eq. (24) may correspond to terms of Eq. (39) of order λ^2 which do not appear to have been studied. The fact that the RPA equations result from the procedure of Sec. II by deleting the second and third terms of Eq. (24) had been noted and rationalized earlier. We have now verified by a more systematic procedure that only the first term results from the expansion of the TDHF matrix to first order in λ. That virtual excitations occur in pairs is still not manifest in the second-order matrix expansion, Eq. (39), to first order in λ.

We illustrate the difference between the approaches of Sec. II and of the TDHF by stressing the restriction under which the perturbation parameter λ is introduced in Eq. (34). A perturbed many-particle wave function Φ is usually expanded in the form $\Phi_0+\lambda\Phi_1+\lambda^2\Phi_2+\cdots$ with few, if any, restrictions on the form of Φ_1 beyond its orthogonality to Φ_0. On the other hand, Eq. (34) implies that Φ_1 is a superposition of determinants each of which differs from Φ_0 in *one column only.* Equation (34) thus amounts to assuming that the excitation of any one electron—if it happens at all—does not affect the other except to higher order. This condition is *unrelated* to the expectation that excitation is itself unlikely owing to weakness of an external disturbance. The TDHF approach thus appears appropriate, at least in essence, to the limit of large systems, as anticipated in the discussion of Eq. (24). It has proven at least reasonably accurate in applications to atoms with six valence electrons, less so in applications to lighter atoms.

An attractive feature of the TDHF approach is the following: Its calculation of the effect of an external field has the formal aspect of a consistent expansion into powers of the parameter λ that characterizes the perturbing field strength. This consideration appears to have encouraged applications, particularly by Dalgarno and coworkers,[11] conducted consistently in the sense of extending the calculation to the perturbations ψ_α and ϕ_α of *all* orbitals α, including those of inner shells where they should be extremely small for frequencies ω in the optical range. The amount of labor inherent in such complete calculations has tended in turn to direct the applications to very light atoms, that is, just to those cases where the method is least appropriate—as noted—owing to the greater role of electron-electron interactions. This remark may account for the modest success of the calculations reviewed by Jamieson.[12] Recent applications have, however, evolved toward the treatment of heavier atoms, disregarding the coupling to inner shells,[30] thus becoming more closely analogous to those developed by Amusia *et al.*[2]

Equivalence of the basic TDHF equations—i.e., Eq. (28) of Ref. 11 or Eq. (1) of Ref. 12—with our Eqs. (21) can be demonstrated, but it requires several adjustments. On the one hand, the separation of spin-angular variables has to be introduced in the TDHF equations and the inhomogeneous terms must be separated; on the other hand, the coupling of all shells and orthognalization corrections must be introduced in the equations of Sec. II (as it is done in Appendix A); finally, various terms have to be regrouped in accordance with the definition of the H^{N-1} Hamiltonian. In Brown's book,[8] the TDHF equations are given initially in their homogeneous form and in the space representation [Eq. (V.18) of Ref. 8], and are then transformed by Eqs. (31) to the RPA second-quantization form (29); Thouless's book[9] follows the same path in a more condensed form.

C. Many-body perturbation theory

This approach may be described for our purposes as an extension and adaptation of the usual Rayleigh-Schrödinger perturbation theory. It deals with the evaluation of observables, such as the dipole transition matrix element between $|\,3p^6\,{}^1S)$ and $|3p^5\Psi\,{}^1P)$ in our example, bypassing any study of the separate wave function of each state; the motive is the same as we indicated at the outset of Sec. II. Our dipole matrix element may be represented as

$$(3p^5\Psi\,{}^1P|U_e^\dagger\Big(\sum_i z_i\Big)U_g|\,3p^6\,{}^1S)\,, \tag{40}$$

where the state symbols indicate single-configuration wave functions constructed with eigenfunctions of the Hartree-Fock Hamiltonian H^N and U_g and $U_e^\dagger$ represent the perturbations of these wave functions due to the residual electron interaction V, i.e., to the interaction not included in H^N.

The MBPT formalism, derived from quantum field theories, provides concepts and rules for analyzing, classifying, and partially evaluating the infinite expansions of the operators

$$U_g=1+\Big(\sum_p |p)\,\frac{1}{E_g-H_{0p}}\,(p|V\Big)+\Big(\sum_{pq}|p)\,\frac{1}{E_g-H_{0p}}\,(p|V|\,q)\,\frac{1}{E_g-H_{0q}}\,(q|V\Big)+\cdots\,,$$

$$U_e^\dagger = 1 + \left(\sum_p V|p)\frac{1}{E+E_g-H_{0p}}(p|\right) + \left(\sum_{pq} V|p)\frac{1}{E+E_g-H_{0p}}(p|V|q)\frac{1}{E+E_g-H_{0q}}(q|\right)+\cdots . \tag{41}$$

Here $|p)$, $|q)$, ... indicate states obtained by lifting *any number* of particles to various eigenstates of H^N; the MBPT stresses that none of the $|p)$, $|q)$, ... may coincide with the ground state. Conservation of angular momentum and parity by V implies that all states $|p)$, $|q)$, ... that contribute to the expansion of U_g in Eq. (40) are ^1S, all those in the expansion of $U_e^\dagger$ are ^1P. In the denominators of the expansion (41), E indicates the excitation energy, as in previous sections, E_g indicates the ground-state energy of the atom, and $H_{0p}, H_{0q}, \ldots$ indicate the eigenvalues of the HF Hamiltonian corresponding to the states $|p)$, $|q)$, ... Rules for the evaluation of these eigenvalues and for the sign of the matrix elements $(p|V|q)$ are provided by the MBPT. The MBPT also shows how to condense certain subsets of terms of the expansion of U_g and $U_e^\dagger$ into more compact forms whose parameters can be evaluated. Beyond this point, one is left to evaluating as many terms as feasible of the joint expansions of $U_e^\dagger$ and U_g, usually only a very few of them. A convenient feature of the MBPT approach is that its steps of approximation are open ended and fairly easily interpreted by diagrammatic analysis, although not easily classified according to successive orders of magnitude.

Consider first the portions of $U_e^\dagger$ containing only matrix elements $(p|V|q)$ that represent either the direct interaction of one $3p$ and one excited electron or the "exchange" interaction which pulls one excited electron back into the $3p$ shell and excites another electron out of this shell. These portions have been taken into account in Sec. II by replacing single-particle eigenfunctions of H^N by the corresponding eigenfunctions of the Hamiltonian $H^{N-1}_{(3p)_2}$ defined by Eq. (9). The corresponding operation is represented in the MBPT by condensing an infinite series of diagrams, representing corrections to a single line—i.e., to an eigenfunction of H^N—into one double line which represents an eigenfunction of H^{N-1} [Fig. 1(a)]. If one discards all other portions of $U_e^\dagger$ and sets $U_g=1$, the whole matrix element, Eq. (40), reduces to a single-particle radial integral $(\psi|r|\chi_{3p})$, where ψ is the solution of Eq. (11a); this condensation is represented diagrammatically by Fig. 1(b).

Owing to the two-particle character of the interaction V, nontrivial operation of U_g on the ground state $|3p^6\,{}^1S)$ in Eq. (40) yields an initial matrix element $(q|V|3p^6\,{}^1S)$ in which the state q is necessarily of the type $|3p^4\Phi_a\Phi_b\,{}^1S)$ considered in Sec. II B; this matrix element is represented by the diagram in Fig. 2(a). (As in Sec. II B, we assume Φ_a and Φ_b to be d rather than s orbitals.) The combination of this matrix element with portions of U_g and $U_e^\dagger$ containing $(p|V|q)$ of the same type considered in the preceding paragraph is again represented diagrammatically in the MBPT by replacing an infinite sum of terms by a single diagram with double lines [Fig. 2(b)]. The resulting contribution to Eq. (40) by expansion terms with $U_g \neq 1$ includes both direct and exchange terms; it is represented graphically in Fig. 2(c) and analytically by an expansion into radial eigenfunctions

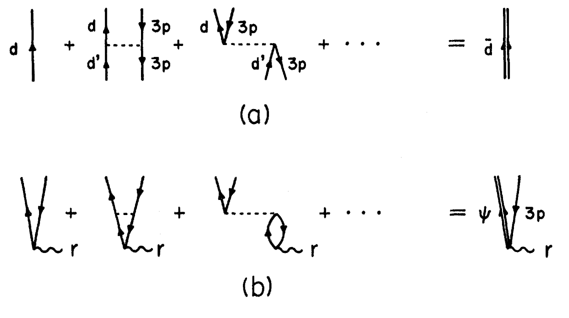

FIG. 1. Diagrams indicating the condensed representation of a series of perturbations (a) to a single excited d state, and (b) to the excited state and vacancy generated by absorption of a photon, indicated by r. The first corrective term represents a simple d-$3p$ Coulomb interaction, the second represents a d-$3p$ recombination which generates another $3p \rightarrow d$ excitation. Dots indicate a series of diagrams representing multiple application of these two basic interactions.

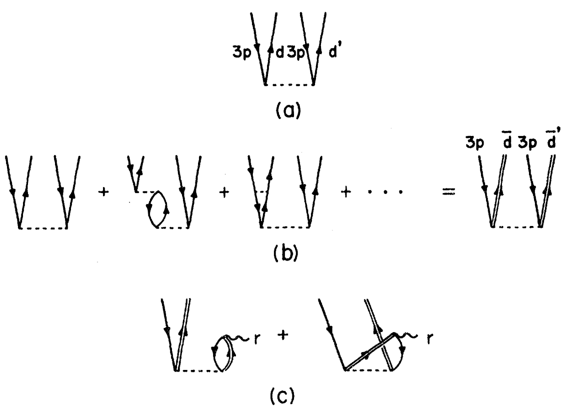

FIG. 2. (a) Elementary process of two-particle virtual excitation. (b) Combination of process 2(a) with the series of perturbations shown in Fig. 1(a). (c) Alternative combinations of photon absorption with the composite process 2(b).

χ_d of H^{N-1}, namely,

$$\sum_{\chi_d} (\chi_{3p}|r|\chi_d)(\epsilon_{3p} - E - H^{N-1}_{(3p)_2})^{-1} \times \sum_k (\chi_d \psi \| V^k \| \chi_{3p}\chi_{3p})\left(\frac{2}{3}\delta_{k1} - \begin{Bmatrix} 2 & 1 & k \\ 2 & 1 & 1 \end{Bmatrix}\right). \quad (42)$$

The occurrence of the operator $H^{N-1}_{(3p)_2}$ instead of eigenvalues H_{0p} in the denominator of this expression is the analytical representation of the condensation of infinite terms from the expansions of U_g and $U_e^\dagger$; the wave function ψ in Eq. (42) is, as above, an eigenfunction of Eq. (11a). The whole expression (42) can be indicated simply as $(\chi_{3p}|r|\phi)$ by setting

$$\phi(r) = \sum_{\chi_d} \chi_a(r)(\epsilon_{3p} - E - H^{N-1}_{(3p)_2})^{-1} \times \sum_k (\chi_d \psi \| V^k \| \chi_{3p}\chi_{3p})\left(\tfrac{2}{3}\delta_{k1} - \begin{Bmatrix} 2 & 1 & k \\ 2 & 1 & 1 \end{Bmatrix}\right); \quad (43)$$

the wave function ϕ so defined is readily seen to be the solution of Eq. (21b). In other words, this procedure leads to a modification of the system of Eqs. (21), in which the first equation—Eq. (11a) which replaces Eq. (21a)—is decoupled from the second. Reducing U_g and $U_e^\dagger$ to the portions discussed thus far reduces the matrix element (40) to the form (16), except for the modification of ψ and ϕ resulting from the partial decoupling of their equations.

To restore the full coupling of Eqs. (21) in the MBPT, one should take into account matrix elements $(p|V|q)$ of Eqs. (41) that shift two excited particles back into the $3p$ shell as represented in Fig. 3(a). Existing MBPT calculations appear to have carried out this step only to lowest order, but this limitation may not have had appreciable consequences, as described below. On the other hand, the MBPT can easily take into account other classes of matrix elements which are not included in the RPA, such as the hole-hole interactions indicated in the diagram of Fig. 3(b). This can be done simply by adding such matrix elements to the eigenvalue H_0 in appropriate denominators of the expansion Eq. (40), or by adding to Eq. (21b) the term of the complete Eq. (19b) with a factor $(\chi_{3p}\chi_{3p}\| V^k \|\chi_{3p}\chi_{3p})$.

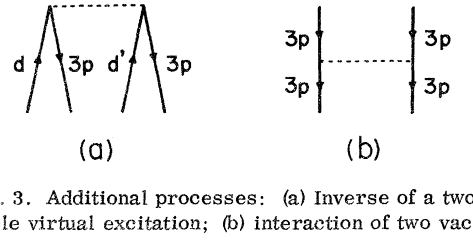

FIG. 3. Additional processes: (a) Inverse of a two-particle virtual excitation; (b) interaction of two vacancies

Only a small portion of the MBPT applications have been directed to the evaluation of transition matrix elements. One of these, by Kelly and Simons,[17] had dealt with the photoionization of Ar; it is thus comparable to the earlier successful RPA work by Amusia *et al.*,[1,2] but differs from it by including the contribution of $3s$ electron excitations from the outset (rather than as an added step) and by leaving Eq. (21a) in effect coupled to its sister equation only to lowest order, as we have just noted. The results agree with experimental data even a little better than those of Ref. 2, suggesting that the differences in the calculation are of little quantitative relevance; we return to this point in Sec. IV.

Other calculations of transition amplitudes by the MBPT have centered on alkali atoms,[16,18] including corrections for long-range core polarization, which are important in this case, and the replacement of algebraic systems by integral equations similar to Eq. (21b) but extended to include the entire group of terms within the second large parentheses of Eq. (19b).[18] These applications have taken particular advantage of the suitability of perturbation treatments to display the separate contributions of different mechanisms and to extend as required to deal with higher-order processes. This flexibility has been utilized, e.g., by Chang *et al.* to treat the double photoionization of Ne,[19] and by Pindzola and Kelly to treat the two-photon ionization of Ar.[31] It is also being utilized to an increasing extent to improve upon RPA treatments, e.g., to adjust ionization thresholds,[2,4,6] to take into account core relaxations,[4] and to include additional terms of the second-order matrix.[32]

IV. DISCUSSION

The formulation and analysis of the Schrödinger equation for transition matrices, which we have developed in Sec. II in the wave-mechanical representation, has proven capable of encompassing several many-body treatments of atomic excitation, of interrelating them, and of setting them in the framework of the Condon-Shortley-Racah theory of spectra. Several new elements of interpretation, contributing to our understanding of transition mechanics, have emerged in the course of this exercise. Thus we seem to have achieved the main goals indicated in Sec. I, even though numerous branches of our unifying treatment remain to be explored.

Emphasis on coupled integro-differential wave equations is common to our approach and to the TDHF calculations of Dalgarno and co-workers,[11] in contrast to the second-quantization approach and to the framework developed earlier by one of us in Secs. 5 and 6 of Ref. 22. This emphasis appears to afford both conceptual and computational advantages. Conceptually, the sign of E in the wave equations (19b) and (21b) makes it manifest that the wave functions ϕ, φ_a, and φ_b, which represent the virtual excitations, are confined to short radial distances. Moreover, all the theories considered here are now seen to deal with the correlation of a single pair of electrons, even though diagrammatic analysis may suggest that simultaneous excitation of several pairs is included. (Incidentally, our treatment points up how the *single* wave function ϕ actually represents an average over the wave functions φ_a and φ_b of *two* virtually excited electrons.) Since the relevant electron correlations embodied in the wave function ϕ are confined within a short range, one may conveniently represent ϕ by one or by a few natural orbitals, and also carry out the calculation by the R-matrix methods that have been developed recently.[33, 34] Irrespective of resort to the R matrix, the computation of the wave-function pair $\psi(r)$ and $\phi(r)$ appears more economical than the solution of the equivalent algebraic problem, which presupposes extended integrations over wave functions of continuum states.

A key conceptual element of our formulation is the Schrödinger equation (23) which should determine the first-order (i.e., single-particle) transition matrix but actually depends also on a second-order matrix. More generally, integration of the N-particle Eq. (1) over the coordinates of $N-n$ particles generates an equation for the nth-order matrix which depends also on the $(n+1)$st-order matrix. Thus we deal with a recursive hierarchy of equations for the matrices of successively higher orders. Only the solution of the full N-particle equation could be accomplished rigorously. Short of this solution, matrices of order $n<N$ can be obtained by some form of approximate truncation of the hierarchy, a situation which is familiar from statistical mechanics. The particular truncation which is performed implicitly by the RPA and TDHF procedures is also familiar from statistical mechanics, in that it retains just that part of the second-order matrix, Eq. (24), which consists of a direct product of two first-order matrices. The general properties of this hierarchy of equations and of the errors to be incurred by possible truncation schemes warrant investigation.

The truncation implied by the RPA provides a high degree of internal consistency. This is demonstrated not only by the cancellation of coupling terms in deriving the normalization equation (25) but especially by the preservation of the oscillator-strength sum rule and of the relationships between the so-called length and velocity dipole formulas.[1,2] It is not immediately apparent to us whether and how this consistency derives from the prescription for truncation of the second-order matrix and hence whether and how it could be preserved when proceeding to higher-order approximations. Obviously relevant to higher approximations is the search for methods of evaluating the terms of Eqs. (19) which cannot be simply annexed to the RPA terms, that is, not only the last groups of terms, which depend on superpositions of φ_a and φ_b other than ϕ, but also those that depend on the coefficients A_k, with $k\neq 1$, B_k, and C_k. The latter terms depend on characteristics of the parentage of the state $|\,3p^4\Phi_a\Phi_b{}^1S)$ that are not incorporated in the coefficient A_1 of the wave function $\phi(r)$.

Broader interest attaches to extending our treatment to the excitation of atoms with open shells, more precisely, to transitions between states neither of which has zero total (or at least orbital) angular momentum. In this case the transition matrices of each order resolve into components with different multipolarities (dipole, quadrupole, etc.). Independent hierarchies of Schrödinger equations govern the components of each multipolarity. An initial survey of this problem is included in a companion paper.[28]

Within the scope of the RPA a question arises that does not seem to have been studied. Solutions of Eqs. (21) have served mainly to calculate the dipole transition matrix elements (16), and attention has centered on the difference of the results thus obtained from those obtained from solution of the simpler HF equation (11a) followed by calculation of the matrix element (5). One may, however, inquire further about the differences between the wave functions $\psi(r)$ obtained by these alternative calculations, particularly about the differences between their phase shifts which would manifest themselves through the angular distribution of photoelectrons. The decoupling of Eq. (21a) from Eq. (21b) which is implied by MBPT calculations (Sec. III C) would be justified if such differences turn out to be negligible. The reasonable agreement with experiment obtained by calculations of angular distributions using RPA dipole elements from Eq. (16) but phase shifts from Eq. (11a) [Sec. 3.6 of Ref. 2] suggests that the phase shifts depend but little on the electron correlations included in the RPA. On the other hand, ${}^1P$ phase shifts calculated for Ar by an R-matrix procedure roughly equivalent to the solution of Eq. (11a) are lower than the experimental values implied by the quantum defects of discrete levels by ~ 0.2 rad.[34]

The analysis presented here involves another obvious approximation besides the truncation of the hierarchy of equations for matrices of successively higher orders, namely, the adoption of a matrix form, Eq. (12), with only two configurations for the ground state and a single one for the excited state. The inaccuracy of this approximation has emerged in our transformation of Eq. (18) into the wave equation (19a) for $\psi(r_1)$ when we could not simply eliminate the dependence on r_1' by factoring out the function $\chi_{3p}(r_1')$. Equation (19a), obtained by projecting the r_1' dependence onto a second factor $\chi_{3p}(r')$, is indeed correct, but it is incomplete in the same sense as Eq. (11a), which contains only a part of the information provided by Eq. (8). An analog of Eq. (11b), which has no manifest solution, would be obtained by projecting Eq. (18) onto a function space orthogonal to $\chi_{3p}(r_1')$; the projection of the first term of Eq. (18) would vanish, and the projection of the second term would have no manifest solution. Here, as in the discussion following Eqs. (11), we regard this inconsistency merely as reflecting inadequacy of the representation of the transition matrix by Eq. (12). Projections of Eq. (18) onto functions orthogonal to $\chi_{3p}(r_1')$ would presumably be solvable if we had extended the representation (12) of the transition matrix, just as Eq. (12) extends Eq. (2). It appears reasonable, indeed, that we meet not just a simple hierarchy of equations but a branching hierarchy, which expands on the one hand toward matrices of successively higher orders and on the other toward matrices that represent the transition with increasing accuracy, in terms of increasing numbers of configurations. Here, as above, a realistic procedure must involve a suitable truncation.

A concluding remark should be made regarding the basic assumption implied by the RPA truncation procedure. We had anticipated that the terms discarded by the RPA, i.e., the terms of Eqs. (19) that are not included in Eqs. (21), would be smaller than the others by a factor reciprocal to the number of electrons in the subshell being excited, i.e., by a factor $\frac{1}{6}$ in our Ar example. A similar understanding of the RPA has often emerged in informal discussions and agrees with the circumstance that the RPA has been introduced for extended media, where the number of equivalent electrons available for excitation is indeed very large. As noted at the end of Sec. II, our expectation seemed to be borne out by the structure of the second-order matrix, Eq. (24), but has not been actually verified by evaluation of the terms discarded by the RPA.

APPENDIX A

The complete Eq. (17) is given by

$$g_{21}(2,\hat{r}_1|w_{00}^{[01]}|1,\hat{r}_1')+g_{12}(1,\hat{r}_1|w_{00}^{[01]}|2,\hat{r}_1')+g_{10}(1,\hat{r}_1|w_{00}^{[01]}|0,\hat{r}_1')+g_{32}(3,\hat{r}_1|w_{00}^{[01]}|2,\hat{r}_1')$$

$$+\sum_{nl,\bar{l}}{}'[g_{\bar{l},nl}(\bar{l},\hat{r}_1|w_{00}^{[01]}|l,\hat{r}_1')+g_{nl,\bar{l}}(l,\hat{r}_1|w_{00}^{[01]}|\bar{l},\hat{r}_1')]=0\,, \qquad \text{(A1)}$$

where $\bar{l}$ indicates the quantum number of excited orbitals and the primed summation includes all spin orbitals nl of the Hartree-Fock ground state of Ar with the exception of the combinations ($nl=3p$, $\bar{l}=2$).

Setting the expression g_{21} to zero gives Eq. (18) and leads to Eq. (19a). The other expressions are as follows:

$$g_{12}=\chi_{3p}(r_1)[(\epsilon_{3p}-E-H^{N-1}_{(3p)2})\,\phi(r_1')+\chi_{3p}(r_1')\sum_k\left(\tfrac{2}{3}\delta_{k1}-\begin{Bmatrix}2&1&k\\2&1&1\end{Bmatrix}\right)(1\|V^k(\chi_{3p},\psi;r_1')\|2)]$$

$$+\frac{1}{A_1}\biggl[\chi_{3p}(r_1)\sum_k\biggl(A_k\begin{Bmatrix}2&1&k\\2&1&1\end{Bmatrix}\chi_{3p}(r_1')(1\|V^k(\chi_{3p},\phi;r_1')\|2)-B_k(1,2)\phi(r_1')(2\|V^k(\chi_{3p},\chi_{3p};r_1')\|1)\biggr)$$

$$-\sum_k C_k(1,2)(1\|V^k(\chi_{3p},\chi_{3p};r_1)\|1)\chi_{3p}(r_1)\phi(r_1')\biggr]$$

$$-\sum_k A_k\begin{Bmatrix}2&1&k\\2&1&1\end{Bmatrix}[(1\|V^k(\varphi_b,\chi_{3p};r_1)\|2)\psi(r_1)\varphi_a(r_1')+(1\|V^k(\varphi_a,\chi_{3p};r_1)\|2)\psi(r_1)\varphi_b(r_1')]$$

$$-\sum_k B_k(2,1)[(1\|V^k(\varphi_b,\psi;r_1)\|1)\chi_{3p}(r_1)\varphi_a(r_1')+(1\|V^k(\varphi_a,\psi;r_1)\|1)\chi_{3p}(r_1)\varphi_b(r_1')]$$

$$-\sum_k C_k(2,1)\chi_{3p}(r_1)[\varphi_a(r_1')(2\|V^k(\psi,\varphi_b;r_1')\|2)+\varphi_b(r_1')(2\|V^k(\psi,\varphi_a;r_1')\|2)]\,, \qquad \text{(A2)}$$

$$g_{10}=-\tfrac{1}{3}\chi_{3p}(r_1)\chi_{3p}(r_1')(1\|V^1(\phi,\chi_{3p};r_1')\|0)+\frac{1}{15^{1/2}}\sum_{SL}\begin{Bmatrix}2&2&L\\1&1&1\end{Bmatrix}\frac{b_{SL}}{A_1}\chi_{3p}(r_1)\phi(r_1')(2\|V^2(\chi_{3p},\chi_{3p};r_1')\|0)$$

$$+\frac{1}{15^{1/2}}\frac{b_{02}}{5}\chi_{3p}(r_1)[\varphi_b(r_1')(2\|V^2(\varphi_a,\psi;r_1')\|0)+\varphi_a(r_1')(2\|V^2(\varphi_b,\psi;r_1')\|0)]\ , \tag{A3}$$

$$g_{32}=-\frac{1}{A_1}\left(\sum_{SL}\begin{Bmatrix}1&3&L\\1&1&2\end{Bmatrix}\begin{Bmatrix}1&3&L\\2&2&1\end{Bmatrix}b_{SL}\right)(3\|V^2(\chi_{3p},\chi_{3p};r_1)\|1)\chi_{3p}(r_1)\phi(r_1')$$

$$-\sum_k A_k\begin{Bmatrix}2&3&k\\2&1&1\end{Bmatrix}[(3\|V^k(\varphi_a,\chi_{3p};r_1)\|2)\psi(r_1)\varphi_b(r_1')+(3\|V^k(\varphi_b,\chi_{3p};r_1)\|2)\psi(r_1)\varphi_a(r_1')]$$

$$+\sum_k\left(\sum_{SL}\begin{Bmatrix}1&1&L\\2&k&2\\1&3&2\end{Bmatrix}b_{SL}\right)[(3\|V^k(\varphi_b,\psi;r_1)\|1)\chi_{3p}(r_1)\varphi_a(r_1')+(3\|V^k(\varphi_a,\psi;r_1)\|1)\chi_{3p}(r_1)\varphi_b(r_1')]\ , \tag{A4}$$

$$g_{\bar{l},nl}=(-1)^l\sum_k\left(\begin{Bmatrix}\bar{l}&k&2\\1&1&l\end{Bmatrix}(\bar{l}\|V^k(\chi_{3p},\chi_{nl};r_1)\|2)\psi(r_1)-\begin{Bmatrix}\bar{l}&k&1\\2&1&l\end{Bmatrix}(\bar{l}\|V^k(\phi,\chi_{nl};r_1)\|1)\chi_{3p}(r_1)\right)\chi_{nl}(r_1')$$

$$-\tfrac{2}{3}[(\bar{l}\|V^1(\chi_{3p},\psi;r_1)\|l)+(\bar{l}\|V^1(\phi,\chi_{3p};r_1)\|l)]\chi_{nl}(r_1)\chi_{nl}(r_1')\ , \tag{A5}$$

$$g_{nl,\bar{l}}=\chi_{nl}(r_1)\left[\sum_k(-1)^k\left(\begin{Bmatrix}\bar{l}&k&1\\2&1&l\end{Bmatrix}\chi_{3p}(r_1')(1\|V^k(\chi_{nl},\psi;r_1')\|\bar{l})+\begin{Bmatrix}\bar{l}&k&2\\1&1&l\end{Bmatrix}\phi(r_1')(2\|V^k(\chi_{nl},\chi_{3p};r_1')\|\bar{l})\right)\right.$$

$$\left.+\tfrac{2}{3}\chi_{nl}(r_1')[(l\|V^1(\chi_{3p},\psi;r_1')\|\bar{l})+(l\|V^1(\phi,\chi_{3p};r_1')\|\bar{l})]\right]\ . \tag{A6}$$

Setting $g_{21}=0$ leads to Eq. (19b); setting the other expressions equal to zero leads to other equations that are inconsistent with Eqs. (19) with the same implications as were noted in the case of Eq. (11b).

APPENDIX B

The system of equations derived from Eq. (29),

$$[E-(\epsilon_n-\epsilon_i)]X_{ni}=\sum_{mj}(nj|\tilde{V}|im)X_{mj}+\sum_{jm}(nm|\tilde{V}|ij)Y_{jm}\ , \tag{B1a}$$

$$-[E+(\epsilon_n-\epsilon_i)]Y_{in}=\sum_{jm}(im|\tilde{V}|nj)Y_{jm}+\sum_{mj}(ij|\tilde{V}|nm)X_{mj}\ , \tag{B1b}$$

is singular in the continuous spectrum where the coefficient of X_{ni}, $E-(\epsilon_n-\epsilon_i)$, has a point of zero. Accordingly, its solution is singular at that point. The equations are treated by Amusia *et al.*[1,2] using the Lippman-Schwinger technique of scattering theory, which yield complex solutions fitted to "outgoing-wave" boundary conditions. Here we outline the variant of that technique which was used in Sec. 6.2 of Ref. 22 and yields real standing-wave solutions that are more appropriate to spectroscopy.

The singularity of χ_{ni} is displayed explicitly by setting

$$X_{ni}=\delta(E-(\epsilon_n-\epsilon_i))A(E)+\mathrm{P}\frac{1}{E-(\epsilon_n-\epsilon_i)}K_{ni}(E), \tag{B2a}$$

where $A(E)$ is a normalization coefficient, P indicates principal-part summation (actually integration) over the pole of $E-(\epsilon_n-\epsilon_i)$, and $K_{ni}(E)$ is a new dependent variable. Equation (B1b) is nonsingular; therefore, the companion of (B2a) has the simpler form

$$Y_{in}=\frac{1}{E+(\epsilon_n-\epsilon_i)}L_{in}(E)\ . \tag{B2b}$$

Substitution of these expressions in Eqs. (B1) yields the nonsingular system

$$K_{ni}(E)=\sum_{mj}(nj|\tilde{V}|im)\delta(E-(\epsilon_m-\epsilon_j))A(E)+\mathrm{P}\sum_{mj}(nj|\tilde{V}|im)\frac{1}{E-(\epsilon_m-\epsilon_j)}K_{mj}(E)$$

$$+\sum_{jm}(nm|\tilde{V}|ij)\frac{1}{E+(\epsilon_m-\epsilon_j)}L_{jm}(E)\,, \tag{B3a}$$

$$-L_{in}(E)=\sum_{jm}(im|\tilde{V}|nj)\frac{1}{E+(\epsilon_m-\epsilon_j)}L_{jm}(E)+\sum_{mj}(ij|\tilde{V}|nm)\delta(E-(\epsilon_m-\epsilon_j))A(E)$$

$$+\mathrm{P}\sum_{mj}(ij|\tilde{V}|nm)\frac{1}{E-(\epsilon_m-\epsilon_j)}K_{mj}(E), \tag{B3b}$$

in which the terms with the coefficient $A(E)$ play the role of inhomogeneity. The dependent variables K_{ni} and L_{in} can now be calculated numerically in terms of the normalization coefficient $A(E)$, reducing the integrations over the continuous spectrum of ϵ_m to discrete sums. The principal-part singularities have been handled straightforwardly in similar problems.[35] The aggregate of the vector components $K_{mj}(E)$ and $L_{jm}(E)$ for a single value of E is equivalent to a single column of the matrix Γ calculated in Refs. 1 and 2. Equation (B3) are equivalent to Eq. (21) of Ref. 2; the notation of Ref. 2 combines the two Eqs. (B3) into a single one and replaces δ functions by an infinitesimal imaginary term in the denominators. The n states in our initial Eq. (29) are eigenstates of H^N. In practice, one should start from the simpler Eqs. (30), where n refers to eigenstates of $H^{N-1}_{(3p)2}$, whereby some terms of the equations of this Appendix vanish.

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