Form-independent third-order transition amplitudes for atoms with one valence electron

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A procedure is given for calculating transition amplitudes that are equal in the length and velocity forms for transitions in atoms with one valence electron within the framework of relativistic many-body perturbation theory starting from the Dirac-Hartree-Fock approximation. This procedure is applied to obtain form-independent second- and third-order dipole matrix elements for the principal transitions in alkali-metal atoms. Comparisons are made with other calculations and with experiment.

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I. INTRODUCTION

In this paper, we describe a procedure for obtaining transition amplitudes that are equal in length form and velocity form in relativistic many-body perturbation theory (MBPT) calculations that start from the Dirac-Hartree-Fock (DHF) approximation. We restrict our attention to atoms that have a single valence electron, and show that although first-second-, and third-order transition amplitudes depend on the form of the transition operator, it is possible to modify the perturbation expansion in such a way that first-order plus second-order and third-order amplitudes are form independent.

Relativistic MBPT is simplest starting from the frozen-core DHF approximation. For atoms with one valence electron, lowest-order valence ionization energies are the eigenvalues of the DHF equations. There are no first-order corrections to the valence energies in accordance with Koopman's theorem. Second-order MBPT corrections, accounting for core polarization, range from 1% for lithium to more than 10% for francium; the resulting transition energies differ from measurement by amounts ranging from 0.1% for lithium to 1% for francium.

An unavoidable consequence of the use of DHF wave functions to calculate transition amplitudes is that length-form and velocity-form amplitudes are different. Although, lowest-order transition matrix elements calculated using local-potential wave functions are independent of the form of the transition operator, and while higher-order MBPT calculations, starting from a local potential are form-independent order-by-order, provided proper attention is given to negative-energy states and appropriate derivative terms are included [1], the same is not true for calculations of transition amplitudes starting from the DHF approximation. We address this problem in the present paper. As a first step, we show that although first-order and second-order amplitudes depend on the form of transition operator, the form dependence is weakened when we consider the sum of the two. We show further that when we replace ''bare'' matrix elements between states in expressions for the second-order amplitude by their ''dressed'' counterparts calculated in the random-phase approximation (RPA), the resulting first- plus second-order transition matrix elements become independent of the form of the transition operator. The form independence of RPA matrix elements is not new; it was noted previously, for example, in Refs. [2] and [3].

The purpose of this paper is to go beyond RPA and illustrate how to obtain form-independent transition amplitudes in third-order MBPT calculations that start from the DHF approximation. An alternative form-independent higher-order extension of the RPA was discussed in Ref. [3] and applied to atoms with one valence electron by Liaw in Ref. [4].

Third-order matrix elements for transitions in one-electron atoms were written out in detail in Ref. [5] and used to evaluate matrix elements for the principal transitions in alkali metals and alkalilike ions in Ref. [8]. The third-order corrections consist of 64 Brueckner-Goldstone diagrams. Of these, the 16 third-order RPA diagrams must be omitted in the present calculation since they are included in the RPA extension of second-order-MBPT described above. Of the remaining, eight Brueckner-orbital diagrams account for core polarization effects, 36 structural radiation diagrams account for the interaction of the photon with virtual orbitals, and four normalization diagrams account for normalization of the state vector and folded diagrams. Later, we show that if first-order matrix elements are replaced by RPA matrix elements in the third-order diagrams, and if a derivative term accounting for the second-order correction to the transition energy is added, the resulting third-order transition amplitude becomes form independent. In fact, form independence can be established separately for the 22 single-excitation and 22 double-excitation contributions to the Brueckner-orbital and structural-radiation diagrams. The normalization diagrams are separately form independent.

In the next section, we outline the theory and describe our calculation. Then, in the final section, we apply form-independent third-order MBPT to evaluate dipole matrix elements for transitions in alkali-metal atoms. Finally, we make comparisons with other calculations and with experimental data. For the principal transitions in alkali-metal atoms, (length-form) DHF dipole matrix elements differ from precise experimental values by amounts ranging from 1% in lithium to 20% in francium. These differences are reduced to 0.5%–10% in the RPA, and to 0.1%–1% in the present form-independent third-order calculations.

II. THEORY

We begin by reviewing briefly the conditions required for form independence of matrix elements. Following the argu-

ments in Sec. IIB of Ref. [6], the change of the transition operator

$$t(\mathbf{r},\omega) = -c\,\boldsymbol{\alpha}\cdot\mathbf{A}(\mathbf{r},\omega) + \phi(\mathbf{r},\omega), \tag{2.1}$$

induced by the gauge transformation

$$\mathbf{A}(\mathbf{r},\omega) \to \mathbf{A}(\mathbf{r},\omega) + \boldsymbol{\nabla}\chi(\mathbf{r},\omega) \tag{2.2}$$

$$\phi(\mathbf{r},\omega) \to \phi(\mathbf{r},\omega) + i\omega\chi(\mathbf{r},\omega), \tag{2.3}$$

is given by

$$\Delta t = \{-c\,\alpha\boldsymbol{\nabla}\chi(\mathbf{r},\omega) + i\omega\chi(\mathbf{r},\omega)\}. \tag{2.4}$$

The unretarded velocity form of the dipole operator is obtained by choosing $\mathbf{A}_v = -\hat{\boldsymbol{\epsilon}}/c$ and $\phi_v = 0$, where $\hat{\boldsymbol{\epsilon}}$ is the photon polarization vector. The corresponding length-form transition operator is obtained from potentials $\mathbf{A}_l = 0$ and $\phi_l = ik\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}$, with $k = \omega/c$. The gauge function $\chi = -\hat{\boldsymbol{\epsilon}}\cdot\mathbf{r}/c$ transforms the length-form dipole operator to velocity form. The generalization to arbitrary multipoles including retardation is given in Refs. [6,7]. Single-particle matrix elements of Δt can be expressed in terms of the gauge function $\chi(\mathbf{r},\omega)$ as

$$\Delta t_{ij}(\omega) = \langle i|\Delta t|j\rangle = -i(\epsilon_i - \epsilon_j - \omega)\chi_{ij} \quad \text{(local potential)}, \tag{2.5}$$

provided the single-particle orbitals for states i and j are obtained in a local potential. For energy-conserving transitions ($\omega = \epsilon_i - \epsilon_j$), the change in t_{ij} induced by a gauge transformation vanishes, explaining why lowest-order matrix elements in a local potential are independent of the form of the electromagnetic field. The identity (2.5) is the fundamental relation used in Ref. [1] to establish the form independence of second- and third-order MBPT calculations starting from a local potential.

If transition matrix elements are calculated using DHF orbitals for states i and j, then the change induced by a gauge transformation is

$$\Delta t_{ij}(\omega) = -i(\epsilon_i - \epsilon_j - \omega)\chi_{ij} - i\sum_{ak}\left[g_{iaak}\chi_{kj} - \chi_{ik}g_{kaaj}\right] \quad \text{(DHF potential)}, \tag{2.6}$$

where g_{ijkl} are two-particle matrix elements of the electron-electron Coulomb interaction. The sum over a on the right-hand side of Eq. (2.6) extends over occupied core orbitals and the sum over k extends over all possible (positive- and negative-energy) orbitals. The sum in Eq. (2.6) arises from the nonlocal exchange term in the DHF potential. It follows from Eq. (2.6) that DHF matrix elements are form dependent even for energy-conserving transitions.

A. Random-phase approximation

In this paragraph, we consider amplitudes T^{RPA}_{an} and T^{RPA}_{na} for transitions between core states and excited states in closed-shell atoms calculated in the random-phase approximation (RPA). We verify that the changes in these amplitudes induced by a gauge transformation satisfy

$$\Delta T^{\mathrm{RPA}}_{an} = -i(\epsilon_a - \epsilon_n - \omega)\chi_{an}, \tag{2.7}$$

$$\Delta T^{\mathrm{RPA}}_{na} = -i(\epsilon_n - \epsilon_a - \omega)\chi_{na}, \tag{2.8}$$

and, consequently, that RPA amplitudes are form independent for energy-conserving transitions. The RPA amplitudes for transitions between core and excited states are defined by the equations [8]:

$$T^{\mathrm{RPA}}_{an} = t_{an} + \sum_{bm}\frac{T^{\mathrm{RPA}}_{bm}\tilde{g}_{amnb}}{\epsilon_b - \epsilon_m - \omega} + \sum_{bm}\frac{\tilde{g}_{abnm}T^{\mathrm{RPA}}_{mb}}{\epsilon_b - \epsilon_m + \omega}, \tag{2.9}$$

$$T^{\mathrm{RPA}}_{na} = t_{na} + \sum_{bm}\frac{T^{\mathrm{RPA}}_{bm}\tilde{g}_{nmab}}{\epsilon_b - \epsilon_m - \omega} + \sum_{bm}\frac{\tilde{g}_{nbam}T^{\mathrm{RPA}}_{mb}}{\epsilon_b - \epsilon_m + \omega}. \tag{2.10}$$

In these equations and in the sequel we use indices a, b, c near the beginning of the alphabet to represent occupied core orbitals, indices m, n, o to represent virtual orbitals, indices i, j, k to represent arbitrary (virtual or occupied) orbitals, and v, w to represent valence orbitals. The notation $\tilde{g}_{ijkl}$ designates antisymmetrized Coulomb matrix elements. From Eqs. (2.9) and (2.10), it follows that the changes $\Delta T^{\mathrm{RPA}}_{an}$ and $\Delta T^{\mathrm{RPA}}_{na}$ induced by a gauge transformation satisfy

$$\Delta T^{\mathrm{RPA}}_{an} = \Delta t_{an} + \sum_{bm}\frac{\Delta T^{\mathrm{RPA}}_{bm}\tilde{g}_{amnb}}{\epsilon_b - \epsilon_m - \omega} + \sum_{bm}\frac{\tilde{g}_{abnm}\Delta T^{\mathrm{RPA}}_{mb}}{\epsilon_b - \epsilon_m + \omega}, \tag{2.11}$$

$$\Delta T^{\mathrm{RPA}}_{na} = \Delta t_{na} + \sum_{bm}\frac{\Delta T^{\mathrm{RPA}}_{bn}\tilde{g}_{nmab}}{\epsilon_b - \epsilon_m - \omega} + \sum_{bm}\frac{\tilde{g}_{nbam}\Delta T^{\mathrm{RPA}}_{mb}}{\epsilon_b - \epsilon_m + \omega}. \tag{2.12}$$

With the aid of Eq. (2.6), it is elementary to verify that Eqs. (2.7) and (2.8) provide a solution to Eqs. (2.11) and (2.12). The uniqueness of the solution follows from the fact that Eqs. (2.11) and (2.12) are a nonsingular system of linear equations.

From these results for core-excited amplitudes, it follows that the generalization of the RPA amplitude to arbitrary transitions given by

$$T^{\mathrm{RPA}}_{ij} = t_{ij} + \sum_{na}\frac{T^{\mathrm{RPA}}_{an}\tilde{g}_{inja}}{\epsilon_a - \epsilon_n - \omega} + \sum_{na}\frac{\tilde{g}_{iajn}T^{\mathrm{RPA}}_{na}}{\epsilon_a - \epsilon_n + \omega} \tag{2.13}$$

satisfies

$$\Delta T^{\mathrm{RPA}}_{ij} = -i(\epsilon_i - \epsilon_j - \omega)\chi_{ij}. \tag{2.14}$$

This is the fundamental identity needed to construct form-independent second- and third-order transition amplitudes.

TABLE I. Iterative solution to the RPA equation (2.13) for the $5s_{1/2}-5p_{1/2}$ transition in Rb, showing the convergence of length-form (L) and velocity-form (V) dipole matrix elements to a gauge-independent value for increasing orders of perturbation theory.

Order	L	V
DHF	4.81 889	4.64 009
2nd	4.59 522	4.61 229
3rd	4.62 324	4.62 061
4th	4.60 236	4.60 910
5th	4.60 834	4.60 883
6th	4.60 522	4.60 654
7th	4.60 632	4.60 643
8th	4.60 581	4.60 604
9th	4.60 601	4.60 603
10th	4.60 592	4.60 596
11th	4.60 596	4.60 596
12th	4.60 594	4.60 595
RPA	4.60 595	4.60 595

B. Form-independent second-order MBPT

The second-order MBPT amplitude, which accounts for shielding of the transition operator by the atomic core, is given by [5]

$$T^{(2)}_{wv}=\sum_{na}\frac{t_{an}\tilde{g}_{wnva}}{\epsilon_a-\epsilon_n-\epsilon_w+\epsilon_v}+\sum_{na}\frac{\tilde{g}_{wavn}t_{na}}{\epsilon_a-\epsilon_n+\epsilon_w-\epsilon_v}. \tag{2.15}$$

On comparing the sum $t_{wv}+T^{(2)}_{wv}$ with the generalized RPA amplitude in Eq. (2.13), it follows that

$$T^{\mathrm{RPA}}_{wv}=t_{wv}+\sum_{na}\frac{T^{\mathrm{RPA}}_{an}\tilde{g}_{wnva}}{\epsilon_a-\epsilon_n-\omega}+\sum_{na}\frac{\tilde{g}_{wavn}T^{\mathrm{RPA}}_{na}}{\epsilon_a-\epsilon_n+\omega}, \tag{2.16}$$

with $\omega=\epsilon_w-\epsilon_v$, is a generalization of the first- plus second-order amplitude that is independent of form for energy-conserving transitions. We adopt T^{RPA}_{wv} here as the form-independent first- plus second-order amplitude.

When the iterative solutions to Eqs. (2.9) and (2.10) are substituted into Eq. (2.16), we recover a subset of terms from first-, second-, and higher-order MBPT that starts from the form-dependent DHF approximation and converges to form-independent RPA amplitude. The convergence of the iteration solution is illustrated in Table I, where we present successive approximations to the length-form and velocity-form dipole matrix elements for the $5s_{1/2}-5p_{1/2}$ transition in rubidium. The convergence becomes slower and slower as we move from one alkali to the next heavier one. Although only 12 iterations are required to achieve convergence to six digits for Rb, 40 iterations are required to achieve the same level of convergence for the $7s_{1/2}-7p_{1/2}$ transition in Fr. Indeed, for the next higher alkali-metal atom (the as yet unobserved element eka-francium, $Z=119$), the perturbation solution to the RPA equations diverges. Since the RPA equations are linear, they can be solved directly using Gaussian elimination for this case.

C. Form-independent third-order MBPT

Explicit formulas for the third-order transition amplitude are written out in Ref. [5] and evaluated for transitions in alkali-metal atoms and alkalilike ions in Ref. [8]. As mentioned in the introduction, the third-order terms may be subdivided into classes according to

$$T^{(3)}=T^{(3)}_{\mathrm{BO}}+T^{(3)}_{\mathrm{SR}}+T^{(3)}_{\mathrm{Norm}}. \tag{2.17}$$

There is, in addition, a third-order RPA term, which is omitted here since it is already included in the form-independent first- plus second-order amplitude given in the previous subsection.

We demonstrate below that with a suitable derivative term, the third-order amplitude is also form independent. The need for derivative terms in MBPT calculations of transition amplitudes was discussed previously in Ref. [1]. The transition operator depends on the transition energy and the transition energy changes order-by-order in an MBPT calculation. The corresponding MBPT amplitude must be modified to account for these changes. For MBPT calculations starting from a DHF potential, there are no first-order corrections to energies. To account for the second-order correction to the transition energy $\delta\omega^{(2)}$, the term

$$T^{(3)}_{\mathrm{deriv}}=\frac{dt_{wv}}{d\omega}\delta\omega^{(2)} \tag{2.18}$$

must be added to the third-order amplitude.

To achieve form independence, it was found necessary to replace all single-particle amplitudes t_{ij} in the expressions for the third-order MBPT amplitude by the corresponding generalized RPA amplitudes T^{RPA}_{ij}. With these replacements, the Brueckner-orbital (BO) correction, which accounts for core polarization, becomes

$$T^{(3)}_{\mathrm{BO}}=\sum_{abmi}\left[\frac{g_{abmv}T^{\mathrm{RPA}}_{wi}\tilde{g}_{miba}}{(\epsilon_i-\epsilon_v)(\epsilon_v+\epsilon_m-\epsilon_a-\epsilon_b)}+\mathrm{c.c.}\right] \tag{2.19}$$

$$+\sum_{amni}\left[\frac{\tilde{g}_{aimn}T^{\mathrm{RPA}}_{wi}g_{mnav}}{(\epsilon_i-\epsilon_v)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}+\mathrm{c.c.}\right]. \tag{2.20}$$

The structural-radiation (SR) correction, which accounts for radiation from virtual states, becomes

$$T^{(3)}_{\mathrm{SR}}=\sum_{abcn}\left[\frac{g_{bavc}T^{\mathrm{RPA}}_{cn}\tilde{g}_{wnba}}{(\epsilon_n-\epsilon_c+\epsilon_w-\epsilon_v)(\epsilon_n+\epsilon_w-\epsilon_a-\epsilon_b)}+\mathrm{c.c.}\right] \tag{2.21}$$

$$+\sum_{abmn}\left[\frac{\tilde{g}_{nwab}T^{\mathrm{RPA}}_{bm}\tilde{g}_{amvn}}{(\epsilon_m-\epsilon_b+\epsilon_w-\epsilon_v)(\epsilon_n+\epsilon_w-\epsilon_a-\epsilon_b)}+\mathrm{c.c.}\right] \tag{2.22}$$

$$+\sum_{amnr}\left[\frac{g_{wrnm}T^{\mathrm{RPA}}_{ar}\tilde{g}_{mnav}}{(\epsilon_r-\epsilon_a+\epsilon_w-\epsilon_v)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}+\mathrm{c.c.}\right] \tag{2.23}$$

$$+\sum_{abmn}\left[\frac{\tilde{g}_{mnav}T^{\mathrm{RPA}}_{bm}\tilde{g}_{awnb}}{(\epsilon_m-\epsilon_b+\epsilon_w-\epsilon_v)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}+\mathrm{c.c.}\right] \tag{2.24}$$

$$+\sum_{abmn}\frac{g_{abvn}T^{\mathrm{RPA}}_{nm}\tilde{g}_{mwab}}{(\epsilon_n+\epsilon_v-\epsilon_a-\epsilon_b)(\epsilon_m+\epsilon_w-\epsilon_a-\epsilon_b)} \tag{2.25}$$

$$+\sum_{abcn}\frac{\tilde{g}_{wnab}T^{\mathrm{RPA}}_{ac}\tilde{g}_{bcnv}}{(\epsilon_n+\epsilon_v-\epsilon_b-\epsilon_c)(\epsilon_n+\epsilon_w-\epsilon_a-\epsilon_b)} \tag{2.26}$$

$$+\sum_{abmn}\frac{g_{mnav}T^{\mathrm{RPA}}_{ab}\tilde{g}_{bwnm}}{(\epsilon_n+\epsilon_m-\epsilon_b-\epsilon_w)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)} \tag{2.27}$$

$$+\sum_{amnr}\frac{\tilde{g}_{wanr}T^{\mathrm{RPA}}_{rm}\tilde{g}_{mnav}}{(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)(\epsilon_r+\epsilon_n-\epsilon_a-\epsilon_w)}. \tag{2.28}$$

The normalization correction, which accounts for wave-function normalization and for folded diagrams, becomes

$$T^{(3)}_{\mathrm{Norm}}=\frac{1}{2}T^{\mathrm{RPA}}_{wv}\left\{\sum_{amn}\frac{\tilde{g}_{vamn}g_{mnav}}{(\epsilon_m+\epsilon_n-\epsilon_a-\epsilon_v)^2}+\sum_{abn}\frac{\tilde{g}_{abnv}g_{nvba}}{(\epsilon_v+\epsilon_n-\epsilon_a-\epsilon_b)^2}+\mathrm{c.c.}\right\}. \tag{2.29}$$

In Eqs. (2.19)–(2.29), the notation ''c.c.'' designates complex conjugation together with interchange of indices v and w. No replacement is required in the derivative term, given by Eq. (2.18).

To establish form independence of the third-order correction, we note first that with the aid of Eq. (2.14), the change induced by a gauge transformation in the ''single excitation'' contributions to $T^{(3)}_{\mathrm{BO}}+T^{(3)}_{\mathrm{SR}}$, which consist of terms (2.19), (2.21)–(2.22) and (2.25)–(2.26), can be reduced to

$$\Delta T^{(3)}_{\mathrm{BO}}|_{\mathrm{sing}}+\Delta T^{(3)}_{\mathrm{SR}}|_{\mathrm{sing}}=-i\chi_{wv}\left[\sum_{abm}\frac{g_{abmw}\tilde{g}_{mwba}}{(\epsilon_w+\epsilon_m-\epsilon_a-\epsilon_b)}-(w\to v)\right]. \tag{2.30}$$

From Ref. [5], one finds that the first term inside the bracket on the right-hand side of this equation is the single-excitation contribution to the second-order valence energy of state w. The bracket, therefore, represents the single-excitation contribution the transition energy $\delta\omega^{(2)}_{\mathrm{sing}}$. In a similar way, one finds that the change induced in the ''double excitation'' contributions to $T^{(3)}_{\mathrm{BO}}+T^{(3)}_{\mathrm{SR}}$, which consist of terms (2.20), (2.23), (2.24), (2.27) and (2.28), can be reduced to

$$\Delta T^{(3)}_{\mathrm{BO}}|_{\mathrm{doub}}+\Delta T^{(3)}_{\mathrm{SR}}|_{\mathrm{doub}}=-i\chi_{wv}\left[\sum_{amn}\frac{\tilde{g}_{avmn}g_{mnav}}{(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}-(v\to w)\right]. \tag{2.31}$$

In this case, the term inside the square bracket on the right-hand side of the equation can be identified with the contribution to the transition energy from double excitations $\delta\omega^{(2)}_{\mathrm{doub}}$. With the derivative term added, Eqs. (2.30) and (2.31) may be rewritten as

$$\Delta T^{(3)}_{\mathrm{BO}}|_{\mathrm{sing}}+\Delta T^{(3)}_{\mathrm{SR}}|_{\mathrm{sing}}+\Delta\frac{dt_{wv}}{d\omega}\delta\omega^{(2)}_{\mathrm{sing}}=0, \tag{2.32}$$

$$\Delta T^{(3)}_{\mathrm{BO}}|_{\mathrm{doub}}+\Delta T^{(3)}_{\mathrm{SR}}|_{\mathrm{doub}}+\Delta\frac{dt_{wv}}{d\omega}\delta\omega^{(2)}_{\mathrm{doub}}=0. \tag{2.33}$$

From these equations, it follows that the combinations

$$T^{(3)}_{\mathrm{BO}}|_{\mathrm{sing}}+T^{(3)}_{\mathrm{SR}}|_{\mathrm{sing}}+\frac{dt_{wv}}{d\omega}\delta\omega^{(2)}_{\mathrm{sing}}$$

and

$$T^{(3)}_{\mathrm{BO}}|_{\mathrm{doub}}+T^{(3)}_{\mathrm{SR}}|_{\mathrm{doub}}+\frac{dt_{wv}}{d\omega}\delta\omega^{(2)}_{\mathrm{doub}}$$

are form independent. Adding these two, we see that the sum of the BO, SR, and derivative terms is form independent. The modified third-order normalization correction, which is proportional to T^{RPA}_{wv} is obviously also form independent.

In Table II, we give a breakdown of the single and double contributions to the dipole matrix element for the $5s$-$5p_{1/2}$ transition in rubidium. Both length-form (L) and velocity-form (V) matrix elements are shown. Row labels refer to the formulas used to evaluate the terms. Length- and velocity-values of the individual terms differ in sign and order of magnitude; moreover, the totals from the BO and SR diagrams differ in L and V forms. When the single- and double-excitation contributions to the derivative term are added, however, L and V contributions come into agreement. The small L-V difference seen for the double excitation contributions arises because we have truncated the double sums.

In the following section, we apply the form-independent expressions developed here to evaluate transitions in alkali-metal atoms.

III. RESULTS AND COMPARISONS

Length and velocity-form matrix elements from our DHF, RPA, and third-order calculations are given in Table III for the principal transitions in alkali-metal atoms. Following the procedure discussed in Ref. [1], the DHF and RPA matrix elements in the tables were obtained by dividing the corresponding amplitudes by the lowest-order transition energies while the third-order matrix elements were obtained by dividing the third-order amplitudes by the second-order transition energies. The DHF results differ in L and V forms as expected. The L and V forms of the RPA matrix elements are identical to the five decimals quoted. There are, however, small L-V differences in the third-order matrix elements primarily of numerical origin. In our numerical work, we employ 40 positive-energy basis functions for each partial wave and truncate the partial-wave sums at $l=8$. The primary

TABLE II. Single- and double-excitation contributions to the third-order dipole matrix element for the $5s_{1/2}-5p_{1/2}$ transition in Rb are given in length-form (L) and velocity-form (V). The numbers in parentheses are equation numbers of the corresponding terms. The term (c.c.) gives the complex conjugate part of the term on the row above.

	Single			Double	
Term	L	V	Term	L	V
(2.19)	−0.0503	0.0715	(2.20)	0.5036	−0.5665
(c.c.)	0.0051	−0.0583	(c.c.)	−0.0190	0.0572
(2.21)	−0.0003	0.0130	(2.23)	0.0201	−0.5058
(c.c.)	0.0003	0.0024	(c.c.)	0.0220	0.5429
(2.22)	0.0000	−0.0084	(2.24)	−0.0233	0.5747
(c.c.)	0.0001	0.0044	(c.c.)	−0.0257	−0.6160
(2.25)	−0.0001	−0.0020	(2.27)	0.0003	−0.0004
(2.26)	0.0001	−0.0022	(2.28)	−0.0184	−0.0439
Sum	−0.0452	0.0203	Sum	0.4597	−0.5579
deriv	0.0655	0.0000	deriv	−1.0176	0.0000
Total	0.0203	0.0203	Total	−0.5580	−0.5579

TABLE III. First-order (DHF), second-order (RPA), and third-order approximations to the dipole matrix elements for the principal transitions in alkali-metal atoms.

	L	V	L	V
Li	$2s-2p_{1/2}$		$2s-2p_{3/2}$	
DHF	3.3644	3.4301	4.7580	4.8510
RPA	3.3505	3.3505	4.7383	4.7383
Third Order	3.3205	3.3205	4.6959	4.6959
Na	$3s-3p_{1/2}$		$3s-3p_{3/2}$	
DHF	3.6906	3.6516	5.2188	5.1632
RPA	3.6474	3.6474	5.1578	5.1578
Third Order	3.5497	3.5497	5.0197	5.0196
K	$4s-4p_{1/2}$		$4s-4p_{3/2}$	
DHF	4.5546	4.4294	6.4391	6.2598
RPA	4.4005	4.4005	6.2221	6.2221
Third Order	4.1316	4.1316	5.8414	5.8413
Rb	$5s-5p_{1/2}$		$5s-5p_{3/2}$	
DHF	4.8189	4.6401	6.8017	6.5399
RPA	4.6059	4.6059	6.5052	6.5052
Third Order	4.2685	4.2684	6.0249	6.0248
Cs	$6s-6p_{1/2}$		$6s-6p_{3/2}$	
DHF	5.2777	5.0371	7.4265	7.0662
RPA	4.9747	4.9747	7.0137	7.0137
Third Order	4.5402	4.5400	6.3892	6.3891
Fr	$7s-7p_{1/2}$		$7s-7p_{3/2}$	
DHF	5.1437	4.8402	7.0903	6.6424
RPA	4.7741	4.7741	6.6268	6.6268
Third Order	4.3236	4.3234	5.9450	5.9448
eka-Fr	$8s-8p_{1/2}$		$8s-8p_{3/2}$	
DHF	4.5306	4.0110	5.5280	4.9964
RPA	3.9878	3.9878	4.9927	4.9927
Third Order	3.6354	3.6346	4.4487	4.4484

TABLE IV. Comparison of third-order MBPT calculations of reduced-matrix elements for the principal transitions with other calculations and with precise experiments.

Element	$ns-np_{1/2}$	$ns-np_{3/2}$	Source
Li ($n=2$)	3.320	4.696	3rd-ord
	3.321	4.696	Br-orb [4]
	3.316	4.691	SD [10]
	3.318	4.693	other [14,15]
	3.317	4.691	other [16–20]
	3.316(3)	4.690(5)	Expt. [11]
Na ($n=3$)	3.550	5.020	3rd-ord
	3.540	5.006	Br-orb [4]
	3.531	4.994	SD [9]
	3.538	5.004	CC [21]
	3.526	4.987	MCHF [22]
	3.524	4.984	MCHF+CI [23]
	3.525(2)	4.984(3)	Expt. [11]
K ($n=4$)	4.132	5.841	3rd-ord
	4.120	5.825	Br-orb [4]
	4.098	5.794	SD [9]
	4.102(5)	5.800(8)	Expt. [11]
Rb ($n=5$)	4.269	6.025	3rd-ord
	4.237	5.978	Br-orb [4]
	4.221	5.956	SD [9]
	4.231(3)	5.977(4)	Expt. [11]
Cs ($n=6$)	4.540	6.389	3rd-ord
	4.474	6.286	Br-orb [4]
	4.478	6.298	SD [9]
	4.499	6.332	MBPT [24]
	4.525	6.370	SD [25]
	4.489(7)	6.324(7)	Expt. [12]
Fr ($n=7$)	4.324	5.945	3rd-ord
	4.256	5.851	SD [9]
	4.279	5.894	MBPT [26]
	4.277(8)	5.898	Expt. [13]

source of error in our third-order matrix elements is this truncation. Although the truncation error is small, it is useful to have a quantitative estimate of its size in a specific case. To this end, we do calculations of the $6s_{1/2}-6p_{1/2}$ dipole matrix element in Cs including partial waves up to values of l that range from six to nine. We find that the matrix element falls off as $1/l^3$ for large l. Assuming this asymptotic behavior, we extrapolate our numerical results for the L- and V-form matrix elements and find $L_\infty=4.53\,869(1)$ and $V_\infty=4.53\,865(1)$. The agreement between L- and V-form matrix elements is improved over the truncated results with $l=8$ by one digit. The residual difference $L_\infty-V_\infty=0.00\,005(2)$ is the contribution from omitted negative-energy states. In previous studies, it was found that negative-energy states contribute principally to V-form matrix elements. Therefore, the form-independent amplitude for the $6s_{1/2}$-$6p_{1/2}$ transition in Cs is $L\equiv L_\infty=4.53\,869(1)$. The numerical accuracy of this result is far greater than warranted, considering that we have neglected contributions from fourth-order perturbation theory that are expected to be of

order 1%. In the tables, we give unextrapolated values of the matrix elements obtained by truncating the partial-wave sums at $l=8$. The effect of truncation slightly increases with increasing Z as can be seen from the tabulated values.

Now let us turn to comparisons with other accurate calculations and with experiment. We present our form-independent third-order matrix elements in Table IV followed by the form-independent Brueckner calculations of Liaw [4]. The values listed from Ref. [4] are averages of L and V matrix elements; the L-V differences are less than 0.2%. These two form-independent generalizations of RPA are in close agreement with one another for Li and Na, but drift apart for the heavier alkalis. All-order single-double calculations have been carried out in Refs. [9,10] for all of the cases considered in Table IV. The L-form SD calculations [9] are generally in good agreement with experiment. The SD matrix elements agree in L and V form to better than 0.1% for Li and Na. For heavier alkalis the L-V differences in the SD calculations increase to the 1% level; the differences are: 0.2% for K, 0.3% for Rb, 0.5% for Cs, and 1% for Fr.

For Li, we also compare our third-order matrix elements with other high-precision calculations [14–20]. All of the calculations for Li cited in the table agree with one another to better than 0.1%. Moreover, these calculations agree with experimentally determined matrix elements [11] to better than 0.1%. The close agreement of the present MBPT calculation with more elaborate calculations and with experiment for Li is somewhat surprising given the fact that the $2s$-$2p$ matrix elements change by 1% from second order to third order. For Na there are, in addition to the Brueckner-orbital and SD calculations discussed earlier, coupled-cluster [21] and multiconfiguration HF [22,23] calculations. No discussion of length-velocity differences is given for these calculations. For cesium, the all-order MBPT result of [24] is in excellent agreement with experiment, however, L-V differences are not discussed. The all-order SD results of Ref. [25] for Cs exhibit L-V agreement and agreement with experiment at the level of 0.7%. As in our third-order calculations, ''bare'' matrix elements were replaced by their RPA counterparts; however, experimental instead of lowest-order transition energies were used in evaluating the RPA amplitudes, and derivative terms were ignored. Furthermore, high-order terms, which need not to be form independent, are included in the SD matrix element contributing to the L-V difference. For Fr, in addition to those mentioned previously, there is the all-order MBPT calculation of [26], but again, no discussion of L-V differences was given.

One interesting aspect of heavy element calculations is that the convergence of the iteration solution of the RPA equations is slow. In the case of Fr, the absolute values of the individual $+\omega$ and $-\omega$ terms in the velocity-form RPA amplitudes from Eq. (2.13) are of approximately the same size as the first-order amplitude, although their smaller sum converges to the full RPA amplitude after many iterations. This fragile convergence breaks down totally in eka-Fr, where already the third-order RPA term becomes very large. To avoid such convergence problems, it is preferable to solve the full RPA equations using Gaussian elimination.

In summary, we have presented a method based on MBPT for obtaining form-independent transition amplitudes through third order for atoms with one valence electron. As a specific application, the method is used to calculate dipole matrix elements for the principal transitions in all alkali-metal atoms. Results are obtained that agree with precise measurements and more elaborate many-body calculations to 1% or better for all cases. The method given here can be generalized in several ways. For example, we could extend it to fourth and higher orders in MBPT, or generalize it to atoms with two or three valence electrons. In the later case, it should be noted that form-independent second-order calculations have been carried out recently for several cases [27–29].

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