Equality of length-form and velocity-form transition amplitudes in relativistic many-body perturbation theory

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Rules for obtaining transition amplitudes that are equal in length form and velocity form, order-by-order in relativistic many-body perturbation theory are presented. Explicit formulas are derived for first-, second-, and third-order amplitudes for transitions between valence states in alkali-metal atoms. Numerical codes are developed to evaluate amplitudes through third order and applied to $3s$-$3p_{1/2}$ and $3s$-$3p_{3/2}$ transitions in sodium and sodiumlike ions. The present calculations for sodiumlike ions are compared with other accurate theoretical calculations.

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I. INTRODUCTION

The transition amplitude $T(\omega)=\langle\Psi_w|t(\omega)|\Psi_v\rangle$ between an exact initial atomic state Ψ_v and an exact final atomic state Ψ_w, where $t(\omega)$ is the frequency-dependent electromagnetic multipole transition operator, is expected to be identical in length form and velocity form for energy-conserving transitions. In nonrelativistic many-body calculations, the equivalence of length-form and velocity-form amplitudes is a consequence of a well-known commutator identity [1]. A similar commutator identity, convenient for relativistic calculations, can be derived using the fact that length-form and velocity-form amplitudes are related by a gauge transformation of the photon field only [2,3]. Since the basic commutator identity used here is obtained with the aid of a limited kind of gauge transformation, we refer to the length-velocity equality as gauge independence. We restrict our attention to the length-velocity equivalence and do not consider acceleration-form transition amplitudes, nor do we consider more general gauge transformations.

Gauge independence of transition amplitudes in quantum field theory and in nonrelativistic quantum mechanics was addressed in Refs. [4–7]. Indeed, a proof of the gauge independence of nonrelativistic transition amplitudes can be found in [5]. These studies were devoted primarily to multiphoton systems, in contrast to the present work, which is concerned with single-photon transitions in many-electron systems. Although single-photon transition amplitudes obtained in the Hartree-Fock (HF) approximation depend on gauge, those obtained in the random-phase approximation (RPA) are gauge independent [8], as are those in variants of the RPA such as the relativistic RPA [9] or the multiconfiguration RPA [10]. At a higher level of precision, gauge-independent amplitudes have been obtained in the Brueckner approximation by Liaw [11] and applied to calculate transition rates in alkali-metal atoms [11] and in Ca^+ [12]. The purpose of the present paper is to derive explicit formulas for transition amplitudes that are gauge-independent order by order in many-body perturbation theory (MBPT) and to apply these formulas through third order to atoms and ions with one valence electron.

Relativistic MBPT calculations of transition amplitudes that are based on the *no-pair* Hamiltonian [13], where contributions from negative-energy states (NES) are omitted, differ in length form and velocity form, as discussed, for example, in [3]. The NES contributions for allowed electric-dipole transitions in the Coulomb gauge scale as $\alpha^2 Z$ for hydrogenlike ions, where Z is the ionic charge [14]. Therefore, for near neutral systems, we expect that the difference between amplitudes calculated in different gauges will be $\propto\alpha^2$, provided the calculations are otherwise exact. Indeed, as we shall see later, length-velocity differences for allowed electric-dipole transitions appear in the fourth or fifth digit in numerical calculations. For forbidden transitions, neglecting NES contributions can lead to significant differences between amplitudes in different gauges. Gauge independence can be restored in such cases by including contributions from the NES. This procedure was followed in the configuration-interaction calculations of Ref. [3].

In either relativistic or nonrelativistic MBPT calculations, Ψ_v and Ψ_w are determined perturbatively, and the transition amplitude $T(\omega)$ is expanded in powers of the interaction potential as

$$T(\omega)=T^{(1)}(\omega)+T^{(2)}(\omega)+T^{(3)}(\omega)+\cdots, \qquad (1.1)$$

where $T^{(1)}(\omega)$ is the first-order matrix element of $t(\omega)$ taken between zeroth-order wave functions; $T^{(2)}(\omega)$ and $T^{(3)}(\omega)$ are the second- and third-order amplitudes written out in detail for the case of atoms with a single valence electron in Ref. [15]. In perturbative calculations, we must include ''derivative'' terms in order to obtain amplitudes that are gauge independent [3]. We base the present analysis of the relativistic MBPT amplitudes on the expressions in [15], but we change the notation used in that reference slightly.[1] In the Appendix, we summarize the formulas from [15] for convenience. The gauge independence of the first two terms in the perturbation expansion was considered in Ref. [3], where it was shown that if we replace ω by $\omega_0=\epsilon_w-\epsilon_v$ in the first-order term $T^{(1)}(\omega)$, then this term becomes independent of

[1]We use T to designate the transition amplitude rather than Z, which was used in [15], in order to avoid confusion with the ionic charge Z.

the gauge of $t(\omega)$. In second order, in addition to replacing ω by ω_0, it is necessary to add a derivative term to preserve gauge independence,

$$T^{(2)}(\omega)\to T^{(2)}(\omega_0)+\left.\frac{dT^{(1)}(\omega)}{d\omega}\right|_{\omega_0}\delta\omega^{(1)},$$

where $\delta\omega^{(1)}$ is the first-order shift in the transition energy. Applying a similar analysis to the third-order term, it becomes clear how to generate derivative terms for higher-order matrix elements. The rule is to expand terms of each order in powers of $\delta\omega=\omega-\omega_0$ and collect all terms of the same order in powers of $1/Z$:

$$\begin{aligned}T&=T^{(1)}(\omega_0)+\frac{dT^{(1)}}{d\omega}\delta\omega+\frac{1}{2}\frac{d^2T^{(1)}}{d\omega^2}(\delta\omega)^2+\cdots+T^{(2)}(\omega_0)\\&\quad+\frac{dT^{(2)}}{d\omega}\delta\omega+\cdots+T^{(3)}(\omega_0)+\cdots,\\&=\mathcal{T}^{(1)}+\mathcal{T}^{(2)}+\mathcal{T}^{(3)}+\cdots,\end{aligned}\tag{1.2}$$

where

$$\mathcal{T}^{(1)}=T^{(1)}(\omega_0),\tag{1.3}$$

$$\mathcal{T}^{(2)}=T^{(2)}(\omega_0)+\frac{dT^{(1)}}{d\omega}\delta\omega^{(1)},\tag{1.4}$$

$$\begin{aligned}\mathcal{T}^{(3)}&=T^{(3)}(\omega_0)+\frac{dT^{(2)}}{d\omega}\delta\omega^{(1)}+\frac{dT^{(1)}}{d\omega}\delta\omega^{(2)}\\&\quad+\frac{1}{2}\frac{d^2T^{(1)}}{d\omega^2}(\delta\omega^{(1)})^2,\end{aligned}\tag{1.5}$$

to third order. The derivatives in the above expressions are defined as

$$\frac{d^nT^{(k)}}{d\omega^n}\equiv\left.\frac{d^nT^{(k)}(\omega)}{d\omega^n}\right|_{\omega_0}\tag{1.6}$$

and powers of $\delta\omega$ as

$$\begin{aligned}\delta\omega&=\delta\omega^{(1)}+\delta\omega^{(2)}+\cdots\\&=(E_w^{(1)}-E_v^{(1)})+(E_w^{(2)}-E_v^{(2)})+\cdots.\end{aligned}\tag{1.7}$$

In calculations based on the Dirac equation, the single-particle multipole transition operator is given in terms of multipole potentials of the electromagnetic field $(\mathbf{A},\phi)$ by

$$t(\mathbf{r},\omega)=-c\,\boldsymbol{\alpha}\cdot\mathbf{A}(\mathbf{r},\omega)+\phi(\mathbf{r},\omega),\tag{1.8}$$

where we denote the quantity h_I of Ref. [3] by t and use atomic units, $e=\hbar=m_e=1$. The gauge transformation

$$\mathbf{A}(\mathbf{r},\omega)\to\mathbf{A}(\mathbf{r},\omega)+\boldsymbol{\nabla}\chi(\mathbf{r},\omega),\tag{1.9}$$

$$\phi(\mathbf{r},\omega)\to\phi(\mathbf{r},\omega)+i\omega\chi(\mathbf{r},\omega),\tag{1.10}$$

induces the change

$$\Delta t=\{-c\,\boldsymbol{\alpha}\boldsymbol{\nabla}\chi(\mathbf{r},\omega)+i\omega\chi(\mathbf{r},\omega)\}\tag{1.11}$$

in the transition operator $t(\omega)$. With the aid of the Dirac equation, single-particle matrix elements of Δt can be expressed in terms of the gauge function $\chi(\mathbf{r},\omega)$ as [3],

$$\Delta t_{ij}(\omega)=\langle i|\Delta t|j\rangle=-i(\epsilon_i-\epsilon_j-\omega)\chi_{ij}.\tag{1.12}$$

Since the first-order matrix element $T^{(1)}=t_{wv}(\omega_0)$ is just the one-particle matrix element of t, and since $\omega_0=\epsilon_w-\epsilon_v$, it follows from Eq. (1.12) that the first-order matrix element is unchanged under the gauge transformation [Eqs. (1.9) and (1.10)]. It should be emphasized that this result depends on the assumption that the interaction potential in the one-particle Dirac equation is local. For calculations based on the nonlocal HF potential, it is a well-known fact that first-order transition amplitude depends on the gauge of the electromagnetic field.

II. SECOND-ORDER TERMS

In this section we discuss in detail the gauge independence of the second-order amplitude in order to clarify some points concerning third-order terms; a similar discussion is given in [3] for atoms with two valence electrons. Formulas for the second-order amplitude are given in Ref. [15] and repeated here in the Appendix for convenience. The second-order amplitude consists of two parts $T^{(2)}=T^{(2)}_{\rm RPA}+T^{(2)}_{\Delta}$ written out in Eqs. (A9) and (A10). The term $T^{(2)}_{\rm RPA}$ accounts in lowest order for shielding of the transition operator by the core electrons; it is the leading term in an expansion of the random-phase approximation to the transition amplitude. The term $T^{(2)}_{\Delta}$ is proportional to $\Delta=V_{\rm HF}-U$, the difference be-

TABLE I. Contributions to the first- and second-order $3s_{1/2}$-$3p_{3/2}$ and $3s_{1/2}$-$3p_{1/2}$ transition amplitudes for sodium in length and velocity forms.

	$3s_{1/2}$-$3p_{3/2}$		$3s_{1/2}$-$3p_{1/2}$	
Term	Length	Velocity	Length	Velocity
$\mathcal{T}^{(1)}$	0.451940	0.451940	−0.318992	−0.318992
$T^{(2)}_{\rm RPA}$	−0.012038	−0.002423	0.008507	0.001799
$T^{(2)}_{\Delta}$	0.083700	−0.077685	−0.059077	0.054351
$(dT^{(1)}/d\omega)\,\delta\omega^{(1)}$	−0.151773	0.000000	0.106717	0.000000
$\mathcal{T}^{(2)}$	−0.080110	−0.080108	0.056147	0.056150

tween the Hartree-Fock potential $V_{\rm HF}$ and the local potential $U(r)$ defining the basic one-electron states; this term vanishes for calculations based on a HF potential. To make the second-order amplitude gauge independent, according to Eq. (1.4), we must set $\omega=\omega_0$ in $T^{(2)}(\omega)$ and add a derivative term. Following the procedure outlined in Sec. I, with the aid of Eq. (1.12), we find that the change in $T^{(2)}$ induced by a gauge transformation is

$$\begin{aligned}
\Delta T^{(2)} &= -i\sum_{na}\ \chi_{an}(g_{wnva}-g_{wnav})+i\sum_{na}\ (g_{wavn}-g_{wanv})\chi_{na}-i\sum_{i\neq v}\ \chi_{wi}(V_{\rm HF}-U)_{iv}+i\sum_{i\neq w}\ (V_{\rm HF}-U)_{wi}\chi_{iv}\\
&= -i\sum_{ia}\ \chi_{ai}(g_{wiva}-g_{wiav})+i\sum_{ia}\ (g_{wavi}-g_{waiv})\chi_{ia}-i\sum_{i}\ \chi_{wi}(V_{\rm HF}-U)_{iv}+i\sum_{i}\ (V_{\rm HF}-U)_{wi}\chi_{iv}-i\,\delta\omega^{(1)}\chi_{wv}\\
&= -i\sum_{ia}\ [\chi_{ai}(g_{wiva}-g_{wiav})-(g_{wavi}-g_{waiv})\chi_{ia}]-i\sum_{ia}\ [\chi_{wi}(g_{iava}-g_{iaav})-(g_{waia}-g_{waai})\chi_{iv}]-i\,\delta\omega^{(1)}\chi_{wv}\\
&= -i\sum_{a}\ ([g\chi(2)]_{wava}-[g\chi(2)]_{waav}-[g\chi(2)]_{wava}+[g\chi(1)]_{waav})-i\sum_{a}\ ([g\chi(1)]_{wava}-[g\chi(1)]_{waav}\\
&\quad -[g\chi(1)]_{wava}+[g\chi(2)]_{waav})-i\,\delta\omega^{(1)}\chi_{wv}\\
&= -i\,\delta\omega^{(1)}\chi_{wv}\,,
\end{aligned}\tag{2.1}$$

where $\delta\omega^{(1)}=(V_{\rm HF}-U)_{ww}-(V_{\rm HF}-U)_{vv}$ is the first-order transition energy and $[g\chi(1)]_{abcd}\overset{\rm def}{=}\Sigma_i\chi_{ai}g_{ibcd}=\Sigma_i g_{abid}\chi_{ic}$. In the above equation, we extended the sum over virtual states n to include contributions from core states, which cancel, and negative-energy states. We then make use of completeness to obtain the expressions in the next-to-last equality. It should be noted that including NES contributions represents an extension of the MBPT formulas given in [15]. The change in the derivative term under a gauge transformation is given by

$$\frac{d\Delta T^{(1)}}{d\omega}=-i\frac{d}{d\omega}(\epsilon_w-\epsilon_v-\omega)\chi_{wv}=i\chi_{wv}\,.\tag{2.2}$$

Therefore, the complete second-order amplitude $\mathcal{T}^{(2)}$ is gauge independent,

$$\begin{aligned}
\Delta\mathcal{T}^{(2)} &= \Delta T^{(2)}+\frac{d\Delta T^{(1)}}{d\omega}\,\delta\omega^{(1)}\\
&= -i\,\delta\omega^{(1)}\chi_{wv}+i\chi_{wv}\delta\omega^{(1)}=0\,.
\end{aligned}\tag{2.3}$$

We notice that the hydrogenlike terms, those containing only $U(r)$ including the derivative component, can be grouped into a gauge-independent contribution. The remaining terms, those containing $V_{\rm HF}$ and the RPA terms, are not gauge independent separately but only when added together. This complication arises because of the exchange parts of these terms, since $[g\chi(1)]_{waav}\neq[g\chi(2)]_{waav}$. In Table I we present a breakdown of the contributions to $\mathcal{T}^{(2)}$ for the $3s_{1/2}$-$3p_{3/2}$ and $3s_{1/2}$-$3p_{1/2}$ transitions in sodium. The table illustrates that although the individual terms $T^{(2)}_{\Delta}$ and $T^{(2)}_{\rm RPA}$ are gauge dependent, the final second-order transition amplitude is indeed independent of gauge; the tiny residual differences in the final amplitudes given in the table are the result of our neglect of contributions from negative-energy states in the numerical calculations.

The calculations used in preparing Table I are based on a local Dirac-Fock-Kohn-Sham potential that takes into account exchange, approximately. The values given in the table are reduced matrix elements of the transition operator, neglecting retardation effects [of relative order $(a_0/\lambda)^2$]. One consequence of the neglect of retardation is that the derivative terms of the velocity-form amplitude vanishes. Moreover, the second derivatives of both length- and velocity-form amplitudes vanish.

As alluded to above, we include only positive-energy states in the sums over intermediate states. The agreement between velocity and length results in the table not only confirms our analysis but also shows that contributions from omitted negative-energy states are very small. With this in mind, we ignore them also in third-order calculations. Finally, a very important point is that the length-velocity agreement provides an excellent test for logical errors, sign errors, and other errors in our analysis and in the associated computer programs.

The gauge-independent perturbation theory above pertains only to many-body calculations based on a local potential; for calculations starting from a nonlocal Hartree-Fock potential, the theory presented above is *not* gauge independent, even in lowest order. This is a consequence of the fact that the Hartree-Fock potential $V_{\rm HF}$ does not commute with the gauge function $\chi(r)$; indeed, Eq. (1.12) is no longer valid. Instead we have

$$\Delta t^{(1)}_{ij}(\omega)=-i\left[(\epsilon_i-\epsilon_j-\omega)\chi_{ij}-\sum_{ka}\ (g_{iaak}\chi_{kj}-\chi_{ik}g_{kaaj})\right].\tag{2.4}$$

TABLE II. Contributions to the third-order transition amplitudes for $3s_{1/2}$-$3p_{3/2}$ and $3s_{1/2}$-$3p_{1/2}$ transitions in Na from the first gauge-invariant subset of terms.

	$3s_{1/2}$-$3p_{3/2}$		$3s_{1/2}$-$3p_{1/2}$	
Term	Length	Velocity	Length	Velocity
Ξ_1	−0.000001	0.004042	0.000000	−0.002846
$(dT^{(2)}_{\rm RPA}/d\omega)\,\delta\omega^{(1)}$	0.004043	0.000000	−0.002846	0.000000
Ξ	0.004042	0.004042	−0.002846	−0.002846

The matrix element between the final and initial states satisfying $\epsilon_w-\epsilon_v=\omega_0$ is not zero,

$$\Delta T^{(1)}\equiv\Delta t_{wv}(\omega_0)=i\sum_{ia}\,[g_{waai}\chi_{iv}-\chi_{wi}g_{iaav}].$$

The difference between length and velocity transition amplitudes in the Hartree-Fock basis, though nonzero, will be one order in $1/Z$ smaller than $T^{(1)}$. With the second-order terms added, this difference becomes even smaller. The remainder in first order is canceled by the RPA remainder, and only terms of second and higher order in $1/Z$ survive. Specifically, in second order for Hartree-Fock calculations only RPA terms contribute,

$$\Delta T^{(2)}_{\rm RPA}=-i\sum_{a}\,\{[g\chi(2)]_{waav}-[g\chi(1)]_{waav}\}+R^{(3)},$$

where $R^{(3)}$ is a residual term of relative order $(1/Z)^2$. Combining the RPA amplitude with the lowest-order amplitude, one finds

$$\Delta T^{(1)}+\Delta T^{(2)}_{\rm RPA}=R^{(3)},$$

which is of relative order $(1/Z)^2$. The third-order contributions will compensate $R^{(3)}$, and so on. Eventually, even the HF result is expected to be gauge independent. In Ref. [16], convergence of the length and velocity amplitudes to each other in the iterated RPA was demonstrated numerically. For the $3s_{1/2}$-$3p_{3/2}$ transition in sodium starting from a HF potential, in first, second, third, and thirty-first order, the length-velocity differences are 6%, 0.7%, 0.4%, and 0.001%, respectively.

III. THIRD-ORDER TERMS

It is possible to separate the complete third-order amplitude into six gauge independent subsets $\mathcal{T}^{(3)}=\Xi+\Delta+\Gamma+\mathcal{N}+\mathcal{S}+\mathcal{D}$. The first subset Ξ consists of the terms on the second line of Eq. (A26) for $T^{(3)}_{\rm SR\text{-}\Delta}$, and their complex conjugates, combined with the derivative term from $T^{(2)}_{\rm RPA}$,

$$\Xi_1=\delta\omega^{(1)}\left\{\sum_{an}\frac{t_{an}\tilde{g}_{wnva}}{(\epsilon_n-\epsilon_a+\omega_0)^2}-\sum_{an}\frac{\tilde{g}_{wavn}t_{na}}{(\epsilon_n-\epsilon_a-\omega_0)^2}\right\},\tag{3.1}$$

$$\frac{dT^{(2)}_{\rm RPA}}{d\omega}\,\delta\omega^{(1)}=-\,\delta\omega^{(1)}\left\{\sum_{an}\frac{dt_{an}}{d\omega}\frac{\tilde{g}_{wnva}}{\epsilon_n-\epsilon_a+\omega_0}+\sum_{an}\frac{\tilde{g}_{wavn}}{\epsilon_n-\epsilon_a-\omega_0}\frac{dt_{na}}{d\omega}\right\},\tag{3.2}$$

where $\omega_0=\epsilon_w-\epsilon_v$. Contributions from these two terms for the $3s$-$3p_{3/2}$ and $3s$-$3p_{1/2}$ transitions in sodium are shown in Table II.

The following subset Δ consisting of eight third-order terms is also independent of gauge:

$$\Delta_1=\sum_{\substack{i\neq w\\ j\neq v}}\frac{\Delta_{wi}t_{ij}\Delta_{jv}}{(\epsilon_i-\epsilon_w)(\epsilon_j-\epsilon_v)},\tag{3.3}$$

$$\Delta_2=-\sum_{i\neq v}\frac{t_{wi}\Delta_{vv}\Delta_{iv}}{(\epsilon_i-\epsilon_v)^2}+\text{c.c.},\tag{3.4}$$

$$\Delta_3=\sum_{\substack{i\neq v\\ j\neq v}}\frac{t_{wi}\Delta_{ij}\Delta_{jv}}{(\epsilon_i-\epsilon_v)(\epsilon_j-\epsilon_v)}+\text{c.c.},\tag{3.5}$$

$$\Delta_4=\sum_{\substack{i\neq w\\ ma}}\frac{\Delta_{wi}t_{am}\tilde{g}_{miav}}{(\epsilon_i-\epsilon_w)(\epsilon_m-\epsilon_a+\omega_0)}+\text{c.c.},\tag{3.6}$$

$$\Delta_5=\sum_{\substack{i\neq v\\ ma}}\frac{\Delta_{iv}t_{am}\tilde{g}_{mwai}}{(\epsilon_i-\epsilon_v)(\epsilon_m-\epsilon_a+\omega_0)}+\text{c.c.},\tag{3.7}$$

$$\frac{dT^{(2)}_{\Delta}}{d\omega}\,\delta\omega^{(1)}=\left[\sum_{i\neq v}\frac{dt_{wi}}{d\omega}\frac{\Delta_{iv}}{(\epsilon_v-\epsilon_i)}+\sum_{i\neq w}\frac{\Delta_{wi}}{(\epsilon_w-\epsilon_i)}\frac{dt_{iv}}{d\omega}\right]\delta\omega^{(1)},\tag{3.8}$$

$$\frac{dT^{(1)}}{d\omega}\,\delta\omega^{(2)}_{\Delta}=\frac{dt_{wv}}{d\omega}\left[\sum_{i\neq v}\frac{\Delta_{vi}\Delta_{iv}}{(\epsilon_i-\epsilon_v)}-\sum_{i\neq w}\frac{\Delta_{wi}\Delta_{iw}}{(\epsilon_i-\epsilon_w)}\right],\tag{3.9}$$

$$\frac{1}{2}\frac{d^2T^{(1)}}{d\omega^2}(\delta\omega^{(1)})^2=\frac{1}{2}\frac{d^2t_{wv}}{d\omega^2}(\delta\omega^{(1)})^2.\tag{3.10}$$

The first three of the terms above Δ_1–Δ_3 are those of order Δ^2 from $T^{(3)}_{\rm BO\text{-}\Delta}$ in Eq. (A25), including complex conjugates. The next two terms, Δ_4 and Δ_5, are those from the first line of $T^{(3)}_{\rm SR\text{-}\Delta}$ in Eq. (A26), including complex conjugates. The

TABLE III. Contributions to the third-order amplitudes for $3s_{1/2}$-$3p_{3/2}$ and $3s_{1/2}$-$3p_{3/2}$ transitions in Na from the second gauge-invariant subset of terms.

	$3s_{1/2}$-$3p_{3/2}$		$3s_{1/2}$-$3p_{1/2}$	
Term	Length	Velocity	Length	Velocity
Δ_1	0.029031	0.036853	−0.020602	−0.026010
Δ_2	0.029994	−0.027834	−0.021132	0.019612
Δ_3	−0.019780	0.018110	0.013983	−0.012489
Δ_4	0.002326	−0.030585	−0.001640	0.021580
Δ_5	0.002062	0.027205	−0.001459	−0.019307
$(dT_\Delta^{(2)}/d\omega)\,\delta\omega^{(1)}$	−0.028109	0.000000	0.019764	0.000000
$(dT^{(1)}/d\omega)\,\delta\omega_\Delta^{(2)}$	0.008228	0.000000	−0.005524	0.000000
$1/2(d^2T^{(1)}/d\omega^2)(\delta\omega^{(1)})^2$	0.000000	0.000000	0.000000	0.000000
Δ	0.023752	0.023750	−0.016611	−0.016613

final three terms are derivative terms. We use the notation $\delta\omega_\Delta^{(2)}$ in Eq. (3.9) to designate the contribution to the second-order transition energy from terms of order Δ^2 in Eq. (A6). The contributions from this subset of terms to third-order matrix elements for the $3s_{1/2}$-$3p_{1/2}$ and $3s_{1/2}$-$3p_{3/2}$ transitions in sodium are listed in Table III. Again, the small residual differences between length and velocity forms in the numerical values are a consequence of neglecting negative-energy contributions.

The third gauge-invariant subset Γ consists of the third-order RPA term $T_{\mathrm{RPA}}^{(3)}$ given in Eq. (A12) combined with the following terms:

$$\Gamma_1=\sum_{nab}\frac{\tilde{g}_{wnav}t_{ab}\Delta_{bn}}{(\epsilon_n-\epsilon_b)(\epsilon_n-\epsilon_a+\omega_0)}+\text{c.c.}, \tag{3.11}$$

$$\Gamma_2=\sum_{nma}\frac{\tilde{g}_{mwav}t_{nm}\Delta_{an}}{(\epsilon_n-\epsilon_a)(\epsilon_m-\epsilon_a+\omega_0)}+\text{c.c.}, \tag{3.12}$$

$$\Gamma_3=-\sum_{nab}\frac{\Delta_{na}\tilde{g}_{awbv}t_{bn}}{(\epsilon_n-\epsilon_a)(\epsilon_n-\epsilon_b+\omega_0)}+\text{c.c.}, \tag{3.13}$$

$$\Gamma_4=\sum_{amn}\frac{\Delta_{na}t_{am}\tilde{g}_{wmvn}}{(\epsilon_n-\epsilon_a)(\epsilon_m-\epsilon_a+\omega_0)}+\text{c.c.}, \tag{3.14}$$

$$\Gamma_5=\sum_{nab}\frac{\tilde{g}_{wnav}t_{bn}\Delta_{ab}}{(\epsilon_n-\epsilon_a+\omega_0)(\epsilon_n-\epsilon_b+\omega_0)}+\text{c.c.}, \tag{3.15}$$

$$\Gamma_6=\sum_{amn}\frac{\Delta_{nm}t_{an}\tilde{g}_{mwav}}{(\epsilon_m-\epsilon_a+\omega_0)(\epsilon_n-\epsilon_a+\omega_0)}+\text{c.c.}, \tag{3.16}$$

$$\Gamma_7=\sum_{\substack{ma\\ i\neq v}}\frac{t_{wi}\tilde{g}_{imva}\Delta_{am}}{(\epsilon_i-\epsilon_v)(\epsilon_m-\epsilon_a)}+\text{c.c.}, \tag{3.17}$$

$$\Gamma_8=\sum_{\substack{na\\ i\neq v}}\frac{t_{wi}\tilde{g}_{iavn}\Delta_{na}}{(\epsilon_i-\epsilon_v)(\epsilon_n-\epsilon_a)}+\text{c.c.}, \tag{3.18}$$

TABLE IV. Contributions to the third-order amplitudes for $3s_{1/2}$-$3p_{1/2}$ and $3s_{1/2}$-$3p_{3/2}$ transitions in Na from the third gauge-invariant subset of terms.

	$3s_{1/2}$-$3p_{3/2}$		$3s_{1/2}$-$3p_{1/2}$	
Term	Length	Velocity	Length	Velocity
Γ_1	−0.000103	−0.000221	0.000073	0.000155
Γ_2	0.000690	0.000199	−0.000487	−0.000143
Γ_3	−0.000124	−0.000214	0.000088	0.000151
Γ_4	0.000374	0.001189	−0.000267	−0.000804
Γ_5	0.003488	0.002380	−0.002462	−0.001711
Γ_6	0.001422	0.001504	−0.001004	−0.001076
Γ_7	0.003977	−0.003469	−0.002804	0.002400
Γ_8	0.003377	−0.001660	−0.002385	0.001164
$(dT^{(1)}/d\omega)\,\delta\omega_{g\Delta}^{(2)}$	−0.012818	0.000000	0.009018	0.000000
$T_{\mathrm{RPA}}^{(3)}$	−0.001730	−0.001158	0.001219	0.000853
Γ	−0.001448	−0.001448	0.000989	0.000989

TABLE V. Contributions of the normalization terms to the $3s_{1/2}$-$3p_{3/2}$ and $3s_{1/2}$-$3p_{1/2}$ transition amplitude in sodium.

	$3s_{1/2}$-$3p_{3/2}$		$3s_{1/2}$-$3p_{1/2}$	
Term	Length	Velocity	Length	Velocity
$T^{(3)}_{\rm Norm}$	−0.002388	−0.002388	0.001687	0.001687
$\mathcal{N}_1$	−0.027409	−0.027409	0.019427	0.019427
$\mathcal{N}_2$	0.001201	0.001201	−0.000850	−0.000850
$\mathcal{N}$	−0.028596	−0.028596	0.020264	0.020264

$$\frac{dT^{(1)}}{d\omega}\,\delta\omega^{(2)}_{g\Delta}=\frac{dt_{wv}}{d\omega}\left\{\sum_{am}\left[\frac{\Delta_{am}\tilde{g}_{mwwa}}{\epsilon_m-\epsilon_a}+\frac{\tilde{g}_{wamw}\Delta_{ma}}{\epsilon_m-\epsilon_a}\right]-\sum_{am}\left[\frac{\Delta_{am}\tilde{g}_{mvva}}{\epsilon_m-\epsilon_a}+\frac{\tilde{g}_{vamv}\Delta_{ma}}{\epsilon_m-\epsilon_a}\right]\right\}. \quad (3.19)$$

The terms Γ_1–Γ_4 are those on the third and fourth lines of $T^{(3)}_{\rm SR\text{-}\Delta}$ in Eq. (A26); Γ_5 and Γ_6 are the entire $T^{(3)}_{\rm RPA\text{-}\Delta}$ contribution from Eq. (A24), while Γ_7 and Γ_8 are the contributions from the terms on the second line of $T^{(3)}_{\rm BO\text{-}\Delta}$ in Eq. (A25). Complex conjugates of all of these terms are included. In Eq. (3.19), $\delta\omega^{(2)}_{g\Delta}$ designates the part of the second-order transition energy that is proportional to the product $g_{abcd}\Delta$ in Eq. (A6). Contributions to third-order matrix elements for $3s_{1/2}$-$3p_{1/2}$ and $3s_{1/2}$-$3p_{3/2}$ transitions in sodium from this subset are listed in Table IV, where they are combined with $T^{(3)}_{\rm RPA}$ to give contributions that differ in length and velocity forms only by omitted negative-energy contributions.

The fourth set of gauge-independent terms $\mathcal{N}$ is the normalization terms $T^{(3)}_{\rm Norm}$ from Eq. (A23) and $T^{(3)}_{\rm Norm\text{-}\Delta}$ from Eq. (A27). This latter term consists of two parts,

$$\mathcal{N}_1=-\frac{1}{2}T^{(1)}\left[\sum_{i\neq v}\frac{\Delta_{vi}\Delta_{iv}}{(\epsilon_i-\epsilon_v)^2}+\text{c.c.}\right], \quad (3.20)$$

$$\mathcal{N}_2-\frac{1}{2}T^{(1)}\left[\sum_{an}\frac{\tilde{g}_{vavn}\Delta_{na}}{(\epsilon_n-\epsilon_a)^2}+\sum_{an}\frac{\Delta_{an}\tilde{g}_{vnva}}{(\epsilon_n-\epsilon_a)^2}+\text{c.c.}\right]. \quad (3.21)$$

TABLE VII. Summary of various contributions to the third-order $3s_{1/2}$-$3p_{3/2}$ and $3s_{1/2}$-$3p_{1/2}$ transition amplitude in sodium.

	$3s_{1/2}$-$3p_{3/2}$		$3s_{1/2}$-$3p_{1/2}$	
Term	Length	Velocity	Length	Velocity
Ξ	0.004042	0.004042	−0.002846	−0.002846
Δ	0.023752	0.023750	−0.016611	−0.016613
Γ	−0.001448	−0.001448	0.000989	0.000989
$\mathcal{N}$	−0.028596	−0.028596	0.020264	0.020264
$\mathcal{S}$	0.001710	0.001710	−0.001220	−0.001219
$\mathcal{D}$	0.019280	0.019276	−0.013550	−0.013548
$\mathcal{T}^{(3)}$	0.018739	0.018735	−0.012973	−0.012973

The contributions of the normalization terms to the third-order amplitude for the $3s_{1/2}$-$3p_{1/2}$ and $3s_{1/2}$-$3p_{3/2}$ transitions in sodium from this subset are listed in Table V. The numerical values of terms are identical in length and velocity gauges, since there are no negative-energy contributions to $T^{(1)}$.

The remaining terms are all bilinear in the Coulomb matrix element g_{ijkl}. These can be grouped into two subsets each of which is individually independent of gauge. The first subset $\mathcal{S}_{gg}$ consists of the single-excitation terms, which consist of the part of $T^{(3)}_{\rm BO}$ given in Eq. (A13) and the parts of $T^{(3)}_{\rm SR}$ given in Eqs. (A15), (A16), (A18), and (A20). These terms lead to a gauge-independent subset when combined with the contribution to the second-order excitation frequency $\delta\omega^{(2)}_s$ from the second term of Eq. (A6) times the derivative of $T^{(1)}$. The second subset $\mathcal{D}_{gg}$ consists of the part of $T^{(3)}_{\rm BO}$ given in Eq. (A14) and the parts of $T^{(3)}_{\rm SR}$ given in Eqs. (A17), (A19), (A21), and (A22); again, these parts combined with the contribution to the second-order excitation frequency $\delta\omega^{(2)}_d$ from the first term of Eq. (A6) times the derivative of $T^{(1)}$ give a gauge-independent subset. We present the contributions to these two subsets from the single and double sums and from the derivative terms in Table VI.

In Table VII we list the subtotals from the six gauge-independent subsets for the $3s_{1/2}$-$3p_{1/2}$ and $3s_{1/2}$-$3p_{3/2}$ transitions in sodium and the resultant third-order amplitude.

TABLE VI. Contributions of the single- and double-excitation terms to the $3s_{1/2}$-$3p_{3/2}$ and $3s_{1/2}$-$3p_{1/2}$ transition amplitude in sodium.

	$3s_{1/2}$-$3p_{3/2}$		$3s_{1/2}$-$3p_{1/2}$	
Term	Length	Velocity	Length	Velocity
$\mathcal{S}_{gg}$	0.005643	0.001710	−0.004004	−0.001219
$(dT^{(1)}/d\omega)\,\delta\omega^{(2)}_s$	−0.003934	0.000000	0.002784	0.000000
$\mathcal{S}$	0.001710	0.001710	−0.001220	−0.001219
$\mathcal{D}_{gg}$	−0.022288	0.019276	0.015739	−0.013548
$(dT^{(1)}/d\omega)\,\delta\omega^{(2)}_d$	0.041568	0.000000	−0.029289	0.000000
$\mathcal{D}$	0.019280	0.019276	−0.013550	−0.013548

TABLE VIII. Perturbation expansion of the $3s_{1/2}$-$3p_{3/2}$ and $3s_{1/2}$-$3p_{1/2}$ transition amplitude in sodium.

	$3s_{1/2}$-$3p_{3/2}$		$3s_{1/2}$-$3p_{1/2}$	
Term	Length	Velocity	Length	Velocity
$\mathcal{T}^{(1)}$	0.451940	0.451940	−0.318992	−0.318992
$\mathcal{T}^{(2)}$	−0.080110	−0.080108	0.056147	0.056150
$\mathcal{T}^{(3)}$	0.018739	0.018735	−0.012973	−0.012973
$\sum_{k=1}^{3}\mathcal{T}^{(k)}$	0.390569	0.390567	−0.275819	−0.275815

Again the small difference between length form and velocity form amplitudes is a result of omitting negative-energy contributions.

IV. SUMMARY AND DISCUSSION

In the preceding two sections, we have presented formulas from relativistic MBPT for length-form and velocity-form amplitudes of dipole transitions between valence states of alkali-metal-like atoms and we have applied these formulas to obtain first-, second-, and third-order amplitudes for transitions in sodium as a specific example. Although we have considered length- and velocity-form amplitudes for electric-dipole transitions in our examples, it should be mentioned that the formalism developed here applies as well to higher multipoles.

The partial contributions to the $3s_{1/2}$-$3p_{1/2}$ and $3s_{1/2}$-$3p_{3/2}$ amplitudes in sodium are shown, along with their sum, in Table VIII. Experimental or theoretical data for transitions are often expressed in terms of line strengths or, equivalently, reduced dipole matrix elements. Reduced matrix elements of the unretarded dipole operator can be obtained from the transition amplitudes defined here by dividing out the transition energy. Therefore, we can define a sequence of approximations of increasing accuracy in $1/Z$ for the dipole matrix elements through the relations,

$$D^{(1)}=\mathcal{T}^{(1)}/\omega_0, \tag{4.1}$$

$$D^{(2)}=(\mathcal{T}^{(1)}+\mathcal{T}^{(2)})/(\omega_0+\delta\omega^{(1)}), \tag{4.2}$$

$$D^{(3)}=(\mathcal{T}^{(1)}+\mathcal{T}^{(2)}+\mathcal{T}^{(3)})/(\omega_0+\delta\omega^{(1)}+\delta\omega^{(2)}). \tag{4.3}$$

In Table IX we apply these formulas to determine first-, second-, and third-order dipole matrix elements for sodiumlike ions with nuclear charges $Z=11-16$. We give length-form dipole matrix elements only, since length-form and velocity-form values agree to all digits quoted. The differences between the second and third approximations to D range from 5% for neutral sodium to 0.4% for Na-like S ($Z=16$).

One expects that third-order MBPT will provide accurate approximations to amplitudes for highly charged ions. That expectation is confirmed for sodiumlike ions, as shown in Table X, where we compare the present third-order dipole matrix elements with a recent all-order single-double (SD) calculation [17] for the Na sequence. We see that differences with the all-order results range from 0.3% for sodium to 0.1% for Na-like S. Our results for neutral Na are in excellent agreement with the Brueckner calculations of Ref. [11], which give 5.006 and 3.540 for the $3s_{1/2}$-$3p_{3/2}$ and $3s_{1/2}$-$3p_{1/2}$ dipole matrix elements, respectively. The present values of these two matrix elements in Na are also in good agreement with the values from a large-scale configuration-interaction (CI) calculation [18], which are 4.993, and 3.530, respectively. The SD and CI calculations, which include correlation corrections beyond third order, are in closer agreement with the recent experimental values [19], 4.984(3) and 3.525(2), respectively, than are the present third-order values or the Brueckner values.

TABLE IX. Order-by-order contributions to length-form $3s_{1/2}$-$3p_{3/2}$ dipole matrix elements for sodiumlike ions. The length-form and velocity-form matrix elements are identical.

	$3s_{1/2}$-$3p_{3/2}$			$3s_{1/2}$-$3p_{1/2}$		
Z	$D^{(1)}$	$D^{(2)}$	$D^{(3)}$	$D^{(1)}$	$D^{(2)}$	$D^{(3)}$
11	4.274	5.295	5.010	3.023	3.743	3.544
12	3.087	3.387	3.367	2.182	2.395	2.381
13	2.474	2.616	2.620	1.748	1.849	1.852
14	2.082	2.163	2.170	1.471	1.528	1.534
15	1.805	1.856	1.863	1.275	1.311	1.317
16	1.597	1.630	1.636	1.128	1.152	1.156

Our all-order expressions for derivative terms should provide the basis for the analysis of length-velocity disagreement in other gauge-dependent theories. Let us consider some particular cases.

(1) If derivative terms are omitted in nth order ($n\geqslant 2$) and ω_0 is substituted in transition-matrix elements, then the length-velocity difference in dipole matrix elements is of second order, even though the first-order amplitude is gauge independent.

(2) If no derivative terms are added but an accurate transition energy is used, then starting from first order, the difference between length and velocity gauges will be of the next-higher order of smallness. This gauge difference in dipole matrix elements is of the same order as the deviation from the exact (all-order) value.

TABLE X. Comparison of third-order dipole matrix elements $D^{(3)}$ for $3s_{1/2}$-$3p_{3/2}$ and $3s_{1/2}$-$3p_{1/2}$ transitions in sodiumlike ions with all-order dipole matrix elements (SD) from [17] .

	$3s_{1/2}$-$3p_{3/2}$		$3s_{1/2}$-$3p_{1/2}$	
Z	$D^{(3)}$	SD	$D^{(3)}$	SD
11	5.010	4.994	3.544	3.531
12	3.367	3.351	2.381	2.369
13	2.620	2.611	1.852	1.845
14	2.170	2.165	1.534	1.523
15	1.863	1.859	1.317	1.314
16	1.636	1.634	1.156	1.154

(3) In Hartree-Fock calculations, regardless of derivative terms, the length-velocity difference in dipole matrix elements is of the next-higher order, provided the experimental frequency is used. Again, the difference provides an estimate of accuracy of that order calculations.

Finally, there is the question of which gauge is preferable in calculations. In gauge-dependent calculations, the length gauge amplitude is often expected to be more reliable because the velocity-form dipole matrix elements implicitly include the lower-order energies while the length-form matrix elements do not. For example, in first order, the velocity transition amplitude $T_v=\omega_0 r$ (for the sake of simplicity, we consider nonrelativistic transition amplitudes v and ωr in which case only the first derivative contributes, and only to the length-gauge amplitude) but the length amplitude is more accurate $T_l=\omega r$ if the frequency is taken from experiment. Dividing T_v by ω_0 we can obtain the same result as in the length case; however, it is not obvious how to do this for higher-order corrections in gauge-dependent potentials or in Dirac-Hartree-Fock (DHF) calculations. In second order, again the velocity-form result $T_v=\omega_1 r^{(1)}+\omega_0 r^{(2)}$ is less accurate than length one $T_l=\omega(r^{(2)}+r^{(1)})$ and the length gauge cannot be obtained with simple division by ω_0 and multiplication by ω. A similar situation exists for higher-order contributions; dividing velocity transition amplitudes by $(\omega_0+\omega_1+\cdots+\omega_n)$ where $n+1$ corresponds to the order of transition amplitude, we can bring the velocity-gauge amplitudes into $n+2$ order of $1/Z$ agreement with length gauge results and, correspondingly, into better agreement with experiment.

In summary, we have presented detailed formulas for obtaining gauge-independent transition amplitudes through third order for atoms with a single valence electron within the framework of relativistic MBPT and, as a practical example, we have applied these formulas to obtain electric-dipole amplitudes for the principal transitions in sodiumlike ions $Z=11-16$.

APPENDIX: BASIC MBPT FORMULAS

In this appendix we summarize the basic formulas from Ref. [15] needed for the present analysis. These formulas are based on the relativistic no-pair Hamiltonian [13], which can be written in second-quantization as

$$H=\sum_i \epsilon_i :a_i^\dagger a_i: +\frac{1}{2}\sum_{ijkl} g_{ijkl}:a_i^\dagger a_j^\dagger a_l a_k: +\sum_{ij} \Delta_{ij}:a_i^\dagger a_j:, \tag{A1}$$

where the sums are restricted to positive-energy states only. In this equation, ϵ_i is the eigenvalue of the one-electron Dirac equation

$$h\,\phi_i=\epsilon_i\phi_i, \tag{A2}$$

with

$$h=c\vec{\alpha}\cdot\vec{p}+\beta c^2+V_{\rm nuc}+U. \tag{A3}$$

The arbitrary central potential $U(r)$ approximates the effect of the electron-electron interaction. The quantity g_{ijkl} in Eq. (A1) is a two-particle Coulomb integral,

$$g_{ijkl}=\langle ij|\frac{1}{r_{12}}|kl\rangle.$$

Later, we represent the antisymmetrized Coulomb integral by $\tilde{g}_{ijkl}=g_{ijkl}-g_{ijlk}$. The difference between the Hartree-Fock potential $V_{\rm HF}$ and the potential $U(r)$ is represented as

$$\Delta_{ij}=(V_{\rm HF}-U)_{ij}.$$

The normal products of creation operators $a_i^\dagger$ and annihilation operators a_j, designated in Eq. (A1) by bracketing operators with colons, are taken with respect to the closed-shell atomic core $|0\rangle$. An atomic state $|v\rangle$ of an atom with one-electron outside the closed core is then given by

$$|v\rangle=a_v^\dagger|0\rangle.$$

The energy of the atom in a state v consists of a core contribution, which is the same for all valence states, and a valence contribution, which changes from state to state. The valence energy can be expanded as

$$E_v=E_v^{(0)}+E_v^{(1)}+E_v^{(2)}+\cdots,$$

where $E_v^{(0)}$ is the eigenvalue of the Dirac equation (A2),

$$E_v^{(0)}=\epsilon_v, \tag{A4}$$

and $E_v^{(1)}$ is the perturbation caused by Δ,

$$E_v^{(1)}=\langle v|\Delta|v\rangle=\Delta_{vv}. \tag{A5}$$

The second-order contribution to the valence energy from Ref. [15] is

$$E_v^{(2)}=-\sum_{amn}\frac{g_{vamn}\tilde{g}_{mnva}}{\epsilon_m+\epsilon_n-\epsilon_v-\epsilon_a}+\sum_{abm}\frac{g_{abmv}\tilde{g}_{mvab}}{\epsilon_m+\epsilon_v-\epsilon_a-\epsilon_b}+\left[\sum_{am}\frac{\Delta_{am}\tilde{g}_{mvva}}{\epsilon_m-\epsilon_a}+\text{c.c.}\right]-\sum_{i\neq v}\frac{\Delta_{vi}\Delta_{iv}}{\epsilon_i-\epsilon_v}. \tag{A6}$$

We use the following conventions for the summation indices:

(1) Indices $a,b,\ldots$, at the beginning of the alphabet range over occupied core orbitals.

(2) Indices m, n, and r, later in the alphabet range over virtual orbitals outside the core.

(3) Indices i, j, k, l range over both core and virtual orbitals.

(4) Indices v and w refer to valence states.

From Ref. [15], we find that the amplitude for a transition from v to w in a one valence electron atom can be written

$$T=T^{(1)}+T^{(2)}+T^{(3)}+\cdots,$$

where the first-order amplitude is simply the matrix element of the transition operator between one-electron valence orbitals

$$T^{(1)}=t_{wv}=\langle w|t|v\rangle. \tag{A7}$$

The second-order amplitude consists of two parts, a random-phase approximation (RPA) correction and a correction from the potential difference Δ,

$$T^{(2)}=T^{(2)}_{\mathrm{RPA}}+T^{(2)}_{\Delta}, \tag{A8}$$

where

$$T^{(2)}_{\mathrm{RPA}}=-\sum_{na}\frac{t_{an}\tilde{g}_{wnva}}{\epsilon_n-\epsilon_a+\omega_0}-\sum_{na}\frac{\tilde{g}_{wavn}t_{na}}{\epsilon_n-\epsilon_a-\omega_0}, \tag{A9}$$

$$T^{(2)}_{\Delta}=\sum_{i\neq v}\frac{t_{wi}\Delta_{iv}}{\epsilon_v-\epsilon_i}+\sum_{i\neq w}\frac{\Delta_{wi}t_{iv}}{\epsilon_w-\epsilon_i}, \tag{A10}$$

with $\omega_0=\epsilon_w-\epsilon_v$.

The third-order correction is considerably more complex; it consists of the eight terms

$$T^{(3)}=T^{(3)}_{\mathrm{RPA}}+T^{(3)}_{\mathrm{BO}}+T^{(3)}_{\mathrm{SR}}+T^{(3)}_{\mathrm{Norm}}+T^{(3)}_{\mathrm{RPA}\text{-}\Delta}+T^{(3)}_{\mathrm{BO}\text{-}\Delta}+T^{(3)}_{\mathrm{SR}\text{-}\Delta}+T^{(3)}_{\mathrm{Norm}\text{-}\Delta}. \tag{A11}$$

The RPA contribution is given by

$$T^{(3)}_{\mathrm{RPA}}=\sum_{abmn}\left[\frac{\tilde{g}_{wnva}t_{bm}\tilde{g}_{amnb}}{(\epsilon_m-\epsilon_b+\omega_0)(\epsilon_n-\epsilon_a+\omega_0)}+\mathrm{c.c.}\right]+\sum_{abmn}\left[\frac{\tilde{g}_{mnab}t_{bm}\tilde{g}_{wanv}}{(\epsilon_m-\epsilon_b+\omega_0)(\epsilon_n-\epsilon_a-\omega_0)}+\mathrm{c.c.}\right]. \tag{A12}$$

The Brueckner-orbital (BO) correction is

$$T^{(3)}_{\mathrm{BO}}=\sum_{abmi}\left[\frac{g_{abmv}t_{wi}\tilde{g}_{miba}}{(\epsilon_i-\epsilon_v)(\epsilon_v+\epsilon_m-\epsilon_a-\epsilon_b)}+\mathrm{c.c.}\right] \tag{A13}$$

$$+\sum_{abmi}\left[\frac{\tilde{g}_{aimn}t_{wi}g_{mnav}}{(\epsilon_i-\epsilon_v)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}+\mathrm{c.c.}\right]. \tag{A14}$$

The structural-radiation (SR) correction is

$$T^{(3)}_{\mathrm{SR}}=\sum_{abcn}\left[\frac{g_{bavc}t_{cn}\tilde{g}_{wnba}}{(\epsilon_n-\epsilon_c+\omega_0)(\epsilon_n+\epsilon_w-\epsilon_a-\epsilon_b)}+\mathrm{c.c.}\right] \tag{A15}$$

$$+\sum_{abcn}\frac{\tilde{g}_{wnab}t_{ac}\tilde{g}_{bcnv}}{(\epsilon_n+\epsilon_v-\epsilon_b-\epsilon_c)(\epsilon_n+\epsilon_w-\epsilon_a-\epsilon_b)} \tag{A16}$$

$$+\sum_{abmn}\left[\frac{\tilde{g}_{mnav}t_{bm}\tilde{g}_{awnb}}{(\epsilon_m-\epsilon_b+\omega_0)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}+\mathrm{c.c.}\right] \tag{A17}$$

$$+\sum_{abmn}\left[\frac{\tilde{g}_{nwab}t_{bm}\tilde{g}_{amvn}}{(\epsilon_m-\epsilon_b+\omega_0)(\epsilon_n+\epsilon_w-\epsilon_a-\epsilon_b)}+\mathrm{c.c.}\right] \tag{A18}$$

$$+\sum_{abmn}\frac{g_{mnav}t_{ab}\tilde{g}_{bwnm}}{(\epsilon_n+\epsilon_m-\epsilon_b-\epsilon_w)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)} \tag{A19}$$

$$+\sum_{abmn}\frac{g_{abvn}t_{nm}\tilde{g}_{mwab}}{(\epsilon_n+\epsilon_v-\epsilon_a-\epsilon_b)(\epsilon_m+\epsilon_w-\epsilon_a-\epsilon_b)} \tag{A20}$$

$$+\sum_{amnr}\left[\frac{g_{wrnm}t_{ar}\tilde{g}_{mnav}}{(\epsilon_r-\epsilon_a+\omega_0)(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)}+\mathrm{c.c.}\right] \tag{A21}$$

$$+\sum_{amnr}\frac{\tilde{g}_{wanr}t_{rm}\tilde{g}_{mnav}}{(\epsilon_n+\epsilon_m-\epsilon_a-\epsilon_v)(\epsilon_r+\epsilon_n-\epsilon_a-\epsilon_w)}. \tag{A22}$$

The Norm correction is

$$T^{(3)}_{\mathrm{Norm}}=\frac{1}{2}T^{(1)}\left\{\sum_{amn}\frac{\tilde{g}_{vamn}g_{mnav}}{(\epsilon_m+\epsilon_n-\epsilon_a-\epsilon_v)^2}+\sum_{abn}\frac{\tilde{g}_{abnv}g_{nvba}}{(\epsilon_v+\epsilon_n-\epsilon_a-\epsilon_b)^2}+\mathrm{c.c.}\right\}. \tag{A23}$$

The RPA-Δ terms are

$$T^{(3)}_{\mathrm{RPA}\text{-}\Delta}=\left\{\sum_{abn}\frac{\tilde{g}_{wnav}t_{bn}\Delta_{ab}}{(\epsilon_n-\epsilon_a+\omega_0)(\epsilon_n-\epsilon_b+\omega_0)}+\sum_{amn}\frac{\Delta_{nm}t_{an}\tilde{g}_{mwav}}{(\epsilon_m-\epsilon_a+\omega_0)(\epsilon_n-\epsilon_a+\omega_0)}+\mathrm{c.c.}\right\}. \tag{A24}$$

The BO-Δ term is given by

$$T^{(3)}_{\mathrm{BO}\text{-}\Delta}=\sum_{\substack{i\neq w\\ j\neq v}}\frac{\Delta_{wi}t_{ij}\Delta_{jv}}{(\epsilon_i-\epsilon_w)(\epsilon_j-\epsilon_v)}+\left\{-\sum_{i\neq v}\frac{t_{wi}\Delta_{vv}\Delta_{iv}}{(\epsilon_i-\epsilon_v)^2}+\sum_{\substack{i\neq v\\ j\neq v}}\frac{t_{wi}\Delta_{ij}\Delta_{jv}}{(\epsilon_i-\epsilon_v)(\epsilon_j-\epsilon_v)}+\sum_{\substack{i\neq v\\ ma}}\frac{t_{wi}\tilde{g}_{imva}\Delta_{am}}{(\epsilon_i-\epsilon_v)(\epsilon_m-\epsilon_a)}+\sum_{\substack{i\neq v\\ na}}\frac{t_{wi}\tilde{g}_{iavn}\Delta_{na}}{(\epsilon_i-\epsilon_v)(\epsilon_n-\epsilon_a)}+\mathrm{c.c.}\right\}. \tag{A25}$$

The SR-Δ correction is

$$T^{(3)}_{\text{SR-}\Delta}=\Bigg\{\sum_{i\neq w,ma}\frac{\Delta_{wi}t_{am}\tilde{g}_{miav}}{(\epsilon_i-\epsilon_w)(\epsilon_m-\epsilon_a+\omega_0)}+\sum_{i\neq v,ma}\frac{\Delta_{iv}t_{am}\tilde{g}_{mwai}}{(\epsilon_i-\epsilon_v)(\epsilon_m-\epsilon_a+\omega_0)}+\sum_{an}\frac{\Delta_{ww}t_{an}\tilde{g}_{wnva}}{(\epsilon_n-\epsilon_a+\omega_0)^2}-\sum_{an}\frac{\Delta_{vv}t_{an}\tilde{g}_{wnva}}{(\epsilon_n-\epsilon_a+\omega_0)^2}-\sum_{nab}\frac{\tilde{g}_{wnva}t_{ab}\Delta_{bn}}{(\epsilon_n-\epsilon_b)(\epsilon_n-\epsilon_a+\omega_0)}+\sum_{amn}\frac{\tilde{g}_{wmva}t_{nm}\Delta_{an}}{(\epsilon_n-\epsilon_a)(\epsilon_m-\epsilon_a+\omega_0)}-\sum_{nab}\frac{\Delta_{na}\tilde{g}_{wavb}t_{bn}}{(\epsilon_n-\epsilon_a)(\epsilon_n-\epsilon_b+\omega_0)}+\sum_{amn}\frac{\Delta_{na}t_{am}\tilde{g}_{wmvn}}{(\epsilon_n-\epsilon_a)(\epsilon_m-\epsilon_a+\omega_0)}+\text{c.c.}\Bigg\}. \tag{A26}$$

The Norm-Δ correction is

$$T^{(3)}_{\text{Norm-}\Delta}=\frac{1}{2}T^{(1)}\Bigg\{-\sum_{an}\frac{\tilde{g}_{vavn}\Delta_{na}}{(\epsilon_n-\epsilon_a)^2}-\sum_{an}\frac{\Delta_{an}\tilde{g}_{vnva}}{(\epsilon_n-\epsilon_a)^2}-\sum_{i\neq v}\frac{\Delta_{vi}\Delta_{iv}}{(\epsilon_i-\epsilon_v)^2}+\text{c.c.}\Bigg\}. \tag{A27}$$

This formula corrects a misprint in the corresponding expression given in Ref. [15].

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