Gauge-invariant approach to the calculation of transition probabilities for many-electron atoms

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Based on field theory, we use a Green's-function formalism to derive an order-by-order approximation to the transition probability of many-electron atoms. The nth-order approximation is obtained by cutting the kernel in the Dyson equation at the nth order of the electron-electron interaction. From the perturbative point of view, each order of approximation is equivalent to the sum of an infinite subset of Feynmann diagrams. The transition probability in each order of approximation is shown analytically to be gauge invariant. Numerical calculations have been done for several atoms. The results of the second-order approximation are, in addition to being gauge invariant, in good agreement with experiment.

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I. INTRODUCTION

For atomic systems, the calculation of transition probabilities is normally more difficult than the calculation of energy levels, mainly because one needs wave functions to calculate transition probabilities. In solving the eigenvalue problem, the eigenvectors (wave functions) are generally less accurate than the eigenvalues (energy levels). It is also easier to determine what kind of corrections should be taken to improve the energy levels. In particular, the perturbative corrections of energy levels can be calculated straightforwardly, but those of wave functions are less obvious and more difficult to realize. For atoms of a few electrons, there exist some methods which can produce very good wave functions [1,2]. The calculation of a transition probability is then as straightforward as in a one-electron system. For atoms with more electrons, the wave functions can only be obtained under some kind of approximation, and an effective vertex with adjustable parameters has to be employed in order to obtain a satisfactory transition probability [3]. A many-body–perturbation-theory calculation for the transition probabilities is also possible. However, current experimental accuracy requires a higher-than-second-order calculation, in which case the many-body perturbation theory becomes tedious and difficult to check [4]. For a particular system, a very large number of configurations (multiconfiguration Hartree-Fock method) can be used to obtain satisfactory results [5].

In Ref. [6], Feldman and Fulton propose a systematic approach for many-electron atoms, based on the field-theoretical formalism. This formalism is suitable for atoms with a nondegenerate core plus or minus one electron. Thus, there are many atoms and ions which can be treated by the formalism. The approach has two properties that make it worth exploring. First, like many-body perturbation theory, the approximations made within the formalism can be improved "order by order." Second, the transition probability in each step of approximations can be shown to be gauge invariant. The first-order approximation in this approach is equivalent to the (frozen-core) Dirac-Fock (DF) approximation. The transition probability in the DF approximation has been explicitly shown to be gauge invariant if a nonlocal term deduced from the formalism is included [7]. A few numerical results for the first-order approximations have been given [8,9]. The second-order approximation, which is called the Brueckner approximation, has been described in Refs. [10] and [11]. In this paper, we give an explicit proof of the gauge invariance of the transition probability in the Brueckner approximation. We choose some transitions in the cases of Lithium and Boron for numerical demonstration for the gauge-invariant (GI) property of the Brueckner approximation. Our results for transition amplitudes are also in good agreement with experimental values.

II. BRUECKNER APPROXIMATION

The formulation of the Brueckner approximation is straightforward from the point of view of the Green's-function formalism for many-body problems. Details about the Green's-function formalism in this context can be found in Refs. [6], [12], and [13]. Here we briefly describe the Brueckner approximation and then prove explicitly that the transition amplitude obtained from the approximation is GI. The Brueckner approximation has also been explained in Refs. [10] and [11].

We start from the definition of the two- and three-point Green's functions:

$$G(12)\equiv -i\langle N,0|T[\Psi(1)\Psi^{\dagger}(2)]|N,0\rangle , \tag{1}$$

$$\Gamma_{\mu}(123)\equiv -\langle N,0|T[\Psi(1)j_{\mu}(3)\Psi^{\dagger}(2)]|N,0\rangle , \tag{2}$$

where $|N,0\rangle$ is the ground state of an N-electron nondegenerate core, Ψ is the electron field, j_{μ} is the current density, T stands for the time-ordered product. The numbers 1, 2, and 3 stand for space-time four-vectors, e.g., $1\equiv(\mathbf{1},t_1)\equiv(\mathbf{r},t_1)$. The above two- and three-point functions satisfy the self-consistent integral equations [6,12] (Dyson equation)

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FIG. 1. Feynman diagrams of the two-point Green's function, $G(12)$, and the electron-electron interaction, $V(12)$.

$$G(12)=G_0(12)+\int d3\int d4\, G_0(13)\Sigma(34)G(42) \tag{3}$$

and

$$\Gamma_\mu(123)=G(13)u_\mu(123)G(32)+\int d4\int d5\,d6\,G(13)G(42)K(3456)\Gamma_\mu(563)\ , \tag{4}$$

respectively, where G_0 is the two-point function under the independent-electron approximation. The local vertex u_μ is given by

$$u_\mu(123)=ie\delta(1-3)\delta(1-2)\gamma_\mu\ , \tag{5}$$

where γ_μ is the standard Dirac gamma matrix. The kernels Σ and K can be given perturbatively in the order of electron-electron Coulomb interaction V:

$$\Sigma=\Sigma^{(1)}+\Sigma^{(2)}+O(V^3)\ , \tag{6}$$

$$K=K^{(1)}+K^{(2)}+O(V^3)\ . \tag{7}$$

Diagrammatically, if we represent $G(12)$ and $V(12)$ as a solid line with an arrow and a dotted line, respectively (Fig. 1), then we have diagrams for kernels up to second order [6] shown in Figs. 2–5. The corresponding algebraic expressions can be read off the diagrams. For example, the second diagram of $\Sigma^{(2)}(12)$ and the first diagram of $K^{(1)}(1234)$ are given respectively by

$$\Sigma_2^{(2)}(12)=\int d3\int d4\, G(13)G(34)G(42)V(14)V(32)\ , \tag{8}$$

and

$$K_1^{(1)}(121'2')=V(12)\delta(1-1')\delta(2-2')\ . \tag{9}$$

FIG. 3. Feynman diagrams of the second-order kernel in Eq. (3): $\Sigma^{(2)}=\Sigma_1^{(2)}+\Sigma_2^{(2)}$.

The wave functions of one-particle (or one-hole) orbitals can be obtained from Eq. (3) by taking residues on both sides in energy space. The transition amplitudes between two one-particle (or one-hole) orbitals satisfy a self-consistent equation which can also be obtained by taking residues on both sides of Eq. (4) in energy space.

A systematic approximation to wave functions and transition amplitudes can be made by cutting the kernels Σ and K order by order in Eqs. (3) and (4) respectively.[1] The choice of an approximate kernel for K, denoted by $\tilde{K}$, has to be based on what approximate kernel for Σ, denoted by $\tilde{\Sigma}$, is used in order to have gauge-invariant transition amplitudes. For example, if we take $\tilde{\Sigma}=\Sigma^{(1)}$, Eq. (3) yields the DF equation. The corresponding GI transition amplitudes can be obtained by taking $\tilde{K}=K^{(1)}$ in Eq. (4). We see that the DF approximation is the first-order approximation in this formalism. The next-order approximation is to take $\tilde{\Sigma}=\Sigma^{(1)}+\Sigma^{(2)}$. The eigenvalue equation satisfied by the wave equations under this approximation is called the Brueckner equation [11]. In what follows, we will prove that the corresponding GI transition amplitudes can be obtained by taking $\tilde{K}=K^{(1)}+K^{(2)}$ in Eq. (4).

The proof of GI of transition amplitudes in the Brueckner approximation follows very closely the proof for the DF approximation given in the Appendix of Ref. [6]. The extension from the DF to Brueckner approximations is much like what Feldman and Fulton had done—also in Ref. [6]—in extending the proof of gauge invariance of transition amplitudes in the random-phase approximation to include up to second-order kernels. In the Brueckner approximation, Eq. (3) is given by

$$G_{\rm Br}(12)=G_0(12)+\int d3\int d4\, G_0(13)[\Sigma^{(1)}(34)+\Sigma^{(2)}(34)]G_{\rm Br}(42)\ . \tag{10}$$

Multiply the equation from the left by G_0^{-1} and from the right by $G_{\rm Br}^{-1}$ and we have (in the form of the Fourier transform)

$$\begin{aligned}G_{\rm Br}^{-1}(\mathbf{12},\omega)&=G_0^{-1}(\mathbf{12},\omega)-[\Sigma^{(1)}(\mathbf{12},\omega)+\Sigma^{(2)}(\mathbf{12},\omega)]\\&=(\omega-H_0)-[\Sigma^{(1)}(\mathbf{12},\omega)+\Sigma^{(2)}(\mathbf{12},\omega)]\\&\equiv\omega-H_{\rm Br}\ ,\end{aligned} \tag{11}$$

where H_0 and $H_{\rm Br}$ are the effective Hamiltonians in the zeroth- and second-order approximations, respectively. The Brueckner equation can then be written as [see Eq. (5) and Ref. [11]]

FIG. 2. Feynman diagrams of the first-order kernel in Eq. (3): $\Sigma^{(1)}=\Sigma_1^{(1)}+\Sigma_2^{(1)}$.

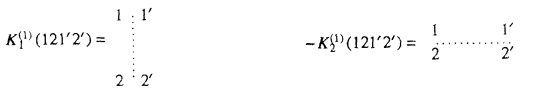

FIG. 4. Feynman diagrams of the first-order kernel in Eq. (4): $K^{(1)}=K_1^{(1)}+K_2^{(1)}$.

[1]It is also possible to cut partial diagrams at each order. See footnote 2 below.

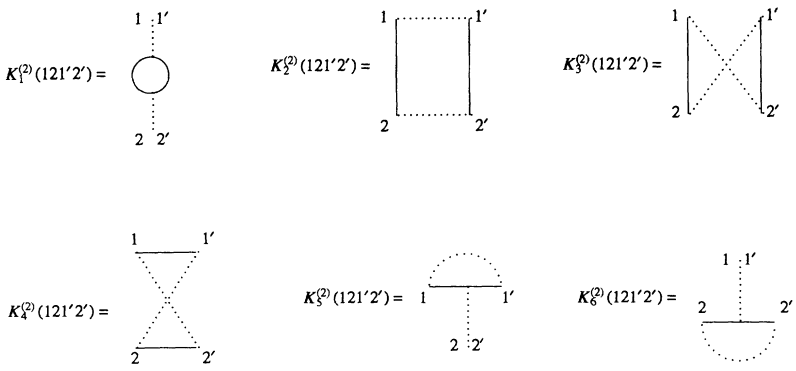

FIG. 5. Feynman diagrams of the second-order kernel in Eq. (4): $K^{(2)}=K_1^{(2)}+K_2^{(2)}+K_3^{(2)}+K_4^{(2)}+K_5^{(2)}+K_6^{(2)}$.

$$\int d2\, G_{\rm Br}^{-1}(12,\omega)\phi_{\rm Br}(2)=\int d2[\omega-H_{\rm Br}(12,\omega)]\phi_{\rm Br}(2) =0 , \quad (12)$$

where $\phi_{\rm Br}$ is the Brueckner wave function.

We define the irreducible vertex $\Lambda_\mu(123)$ as

$$\Gamma_\mu(123)=\int d1'\int d2' G(11')\Lambda_\mu(1'2'3)G(2'2) . \quad (13)$$

The transition amplitudes between one-particle states ϕ_m and ϕ_n are given by [6]

$$\Lambda_{mn}(\omega)=\int d1\int d2\int d3\,\phi_m^\dagger(1)\Lambda_\mu(123)\phi_n(2)A^\mu_{\omega LM}(3) , \quad (14)$$

where $A^\mu_{\omega LM}$ is the photon amplitude with definite angular momentum L, projection M, and energy ω. From Eqs. (3) and (4), the Fourier transform of the irreducible vertex Λ_μ under the Brueckner approximation satisfies the following equation [6]:

$$\begin{aligned}
&\Lambda_\mu^{\rm Br}(12z,\omega_1,\omega_2)\\
&=u_\mu(12z)+\int d3\int d4\int d\omega' G(13,\omega')G(42,\omega'-\omega_1+\omega_2)V(12)\Lambda_\mu^{\rm Br}(34z,\omega',\omega'-\omega_1+\omega_2)\\
&\quad-\int d3\int d4\int d\omega' G(53,\omega')G(45,\omega'-\omega_1+\omega_2)V(15)\delta(1-2)\Lambda_\mu^{\rm Br}(34z,\omega',\omega'-\omega_1+\omega_2)\\
&\quad+\int d3\int d4\int d5\int d6\int d\omega'\int d\omega''\\
&\quad\times\{G(56,\omega_1-\omega'+\omega'')G(65,\omega'')V(15)V(26)G(13,\omega')G(42,\omega'-\omega_1+\omega_2)\Lambda_\mu^{\rm Br}(34z,\omega',\omega'-\omega_1+\omega_2)\\
&\qquad+G(12,\omega_1-\omega'+\omega'')G(65,\omega'')V(15)V(26)G(53,\omega')G(46,\omega'-\omega_1+\omega_2)\Lambda_\mu^{\rm Br}(34z,\omega',\omega'-\omega_1+\omega_2)\\
&\qquad+G(12,\omega_2+\omega'-\omega'')G(65,\omega'')V(52)V(16)G(53,\omega')G(46,\omega'-\omega_1+\omega_2)\Lambda_\mu^{\rm Br}(34z,\omega',\omega'-\omega_1+\omega_2)\\
&\qquad+G(15,\omega_2+\omega'-\omega'')G(62,\omega'')V(52)V(16)G(53,\omega')G(46,\omega'-\omega_1+\omega_2)\Lambda_\mu^{\rm Br}(34z,\omega',\omega'-\omega_1+\omega_2)\\
&\qquad+G(15,\omega_1-\omega'+\omega'')G(56,\omega'')V(16)V(25)G(63,\omega')G(42,\omega'-\omega_1+\omega_2)\Lambda_\mu^{\rm Br}(34z,\omega',\omega'-\omega_1+\omega_2)\\
&\qquad+G(65,-\omega_1+\omega'+\omega'')G(52,\omega'')V(15)V(26)G(13,\omega')G(46,\omega'-\omega_1+\omega_2)\Lambda_\mu^{\rm Br}(34z,\omega',\omega'-\omega_1+\omega_2)\} . \quad (15)
\end{aligned}$$

The first term on the right-hand side of Eq. (15) is the local vertex; the second and third terms come from the first-order kernel $K^{(1)}$; the other terms come from the second-order kernel $K^{(2)}$. Note that $\Lambda_\mu^{\rm Br}(123,\omega_1,\omega_2)$ depends on the photon energy ω, the difference of ω_1 and ω_2, only and not on ω_1 or ω_2 independently. This can be checked easily by showing that $\Lambda_\mu^{\rm Br}(12z,\omega_1+\bar\omega,\omega_2+\bar\omega)$ has the same expression as $\Lambda_\mu^{\rm Br}(12z,\omega_1,\omega_2)$. The integrations over ω' and ω'' in Eq. (15) can be carried out to write Λ_μ in terms of summations over one-particle and one-hole Brueckner wave functions. The complete expression for transition amplitudes in the Brueckner approximation resulting from integrations over ω' and ω'' is given in Eqs. (2) and (4) of Ref. [10]. We can put this expression in the following form [11]:

$$\Lambda_{mn}^{\rm Br}(\omega)=\int d1\int d2\int d3\,\phi_m^{\dagger\rm Br}(1)\Lambda_\mu^{\rm Br}(123)\phi_n^{\rm Br}(2)A^\mu_{\omega LM}(3) =u_{mn}+Z_{mn}^{(1)}(\Lambda)+Z_{mn}^{(2)}(\Lambda) . \quad (16)$$

In Ref. [11] where alkali-metal atoms are considered, the local term u_{mn} and the random-phase-approximation–type contribution $Z_{mn}^{(1)}$ are included self-consistently, while the second-order contribution $Z_{mn}^{(2)}$ is treated as a perturbation. In this paper we solve Eq. (16) self-consistently using the finite basis method.

Let k^μ be the four momentum of the photon. The "gauged" local vertex $k^\mu u_\mu$ is given by [6]

$$k^\mu u_\mu(12z)=e[\delta(z-2)G_0^{-1}(1z,\omega_1) -\delta(1-z)G_0^{-1}(z2,\omega_2)] . \quad (17)$$

We now show that the gauged effective vertex in the Brueckner approximation $k^\mu \Lambda_\mu^{\rm Br}$ can be expressed by (generalized Ward-Takahashi identity)

$$k^\mu \Lambda_\mu^{\rm Br}(12z,\omega_1,\omega_2)=e[\delta(z-2)G_{\rm Br}^{-1}(1z,\omega_1) -\delta(1-z)G_{\rm Br}^{-1}(z2,\omega_2)] . \quad (18)$$

We saturate both sides of Eq. (15) with k^μ and use expressions of Eqs. (17) and (18) for $k^\mu u_\mu$ and $k^\mu \Lambda_\mu^{\rm Br}$ which appear on the right-hand side of Eq. (15) and show that Eq. (15) is satisfied self-consistently. When saturated with k^μ, the local term on the right is given by Eq. (17). The two first-order terms give

$$-e\{\delta(z-2)\Sigma^{(1)}(1z,\omega_1)-\delta(1-z)\Sigma^{(1)}(z2,\omega_2)\} .$$

The last six second-order terms yield

$$-e\{\delta(z-2)\Sigma^{(2)}(1z,\omega_1)-\delta(1-z)\Sigma^{(2)}(z2,\omega_2)\} .$$

Putting all these results together we have

$$\begin{aligned} k^\mu \Lambda_\mu^{\rm Br}(12z,\omega_1,\omega_2)&=e\delta(z-2)[G_0^{-1}(1z,\omega_1)-\Sigma^{(1)}(1z,\omega_1)-\Sigma^{(2)}(1z,\omega_1)] \\ &\quad -e\delta(1-z)[G_0^{-1}(z2,\omega_2)-\Sigma^{(1)}(z2,\omega_2)-\Sigma^{(2)}(z2,\omega_2)] \\ &=e\{\delta(z-2)G_{\rm Br}^{-1}(1z,\omega_1)-\delta(1-z)G_{\rm Br}^{-1}(z2,\omega_1)\} . \end{aligned} \quad (19)$$

which confirms[2] Eq. (18).

With the help of Eq. (18) the gauge invariance of transition amplitudes in the Brueckner approximation is readily seen; if we replace the photon amplitude $A_{\omega LM}^\mu$ by photon four momentum k^μ in the expression of the transition amplitude [Eq. (16)], we have

$$\begin{aligned} &\int d1 \int d2\, \phi_i^{\rm br*}(1)[k^\mu \Lambda_\mu^{\rm Br}(12z,\omega_i,\omega_f)]\phi_f^{\rm Br}(2) \\ &=e\left\{\int d1[\phi_i^{\rm Br*}(1)G_{\rm Br}^{-1}(1z,\omega_i)]\phi_f^{\rm Br}(z)\right\} \\ &\quad -e\left\{\int d2\, \phi_i^{\rm Br*}(z)[G_{\rm Br}^{-1}(z2,\omega_f)\phi_f^{\rm Br}(2)]\right\} \\ &=0 \end{aligned} \quad (20)$$

[because of Eq. (12)].

III. NUMERICAL DEMONSTRATION

We use the B-spline method [14] to solve the Brueckner equation, Eq. (12). In order to be able to calculate the transition amplitudes in the Brueckner approximation, Eq. (16), we have to obtain the complete set of Brueckner orbitals. In the case of the DF approximation, all orbitals with the same κ [$\kappa=l(-l-1)$ if $j=l-\frac{1}{2}$ $(l+\frac{1}{2})$] satisfy the same DF equation and thus can be solved simultaneously in the finite bases method [8]. For the Brueckner equation there are energy-dependent terms due to $\Sigma^{(2)}$ [Eq. (5) and Ref. [11]]. All wave functions have to be solved separately. In Ref. [11], a specific approximation is made to generate an approximately complete set of the Brueckner orbitals. Namely, for all orbitals with the same κ, a single energy level is chosen for $\Sigma^{(2)}(\omega)$. We choose this energy to be the lowest one-particle energy level for two reasons. First, we are concerned with the transitions between the lowest one-particle states of each κ. Thus these lowest one-particle wave functions have to be solved as accurately as possible. Second, one sees that there is at least one one-hole energy level present in the energy denominator [Eq. (5) and Ref. [11]]. If the energy levels of one-particle bound states are much less than any one-hole energy level (in absolute value), the choice causes little error for bound states. The approximation for choosing a single energy level for $\Sigma^{(2)}(\omega)$ in solving the Brueckner equation is acceptable for alkali-metal atoms [11] and boron (see below). But it is not always applicable in the latter atom, as we will discuss.

For the purpose of demonstration we study the transitions $2p\rightarrow 2s, 2p\rightarrow 3s$ of Li I, and $2p\rightarrow 3s$ of B I. We first calculate the transition amplitudes in the DF approximation. Results are listed in columns 3 and 4 of Table I. The $2p\rightarrow 2s$ transition amplitudes for Li I have been calculated by Fulton and Johnson [7] using a different numerical method. Our results agree with theirs. We then solve for the Brueckner orbitals using the approximation described above. Once having the complete orbitals, we integrate out the energies in Eq. (15) and write the transition amplitudes $\Lambda_{mn}^{\rm Br}(\omega)$ and all the matrix elements $\Lambda_{st}^{\rm Br}(\omega)$ in terms of summations over one-particle and one-hole states to form a set of coupled linear equations. For the cases of Li I and B I with cores $1s^2$ and $1s^2 2s^2$ respectively, we keep all matrix elements between wave functions of orbital angular momentum smaller than three. Results of transition amplitudes in length and velocity forms agree with each other within 0.5% (see Table I). For Li I—in fact, for all alkali-metal atoms [11]—the second-order contributions are small in either gauge and thus can be treated as a perturbation (column 7, Table I). In the case of boron, which has a closed subshell instead of closed shell, treating the second-order contribution as a perturbation would result in a 2.5% difference between

[2]Note that the gauge invariance of transition amplitude can also be obtained by choosing a subset from the diagrams of the kernel K if the kernel Σ in the Brueckner equation is cut consistently. For example, choosing the kernel in the Brueckner equation to be $\Sigma_1^{(1)}+\Sigma_1^{(2)}$, the kernel in the Eq. (4) can be chosen to be $K_1^{(1)}+K_1^{(2)}+K_2^{(2)}+K_3^{(2)}$, or simply $K_1^{(1)}+K_1^{(2)}$ (because the effects of $K_2^{(2)}$ and $K_3^{(2)}$ cancel out).

TABLE I. Transition amplitudes in the Dirac-Fock and Brueckner approximations for Li I and B I. l,v stand for length and velocity forms, respectively. The contribution comes from the first-order kernel and is conventionally called the random-phase-approximation (RPA) contribution. For the Dirac-Fock approximation, column 4 is gauge invariant (GI). For the Brueckner approximation, the transition amplitude is GI only when the contribution from the second order is included self-consistently. In the case of Li I, the second-order contribution is small and can be well accounted for by perturbation (column 7). Transition amplitudes are given in a.u.

		Dirac-Fock		Brueckner				
Transition	Form	Local	Local + RPA	Local	Local + RPA	2nd	GI	Experiment
				Li ($Z=3$, core $=1s^2$)				
$2s\rightarrow 2p_{1/2}$	l	3.364	3.350	3.335	3.321	0.0007	3.322	3.305[a]
	v	3.430	3.350	3.404	3.321	−0.0004	3.321	
$2s\rightarrow 2p_{3/2}$	l	4.758	4.738	4.717	4.697	0.0009	4.698	4.674[a]
	v	4.850	4.738	4.815	4.697	−0.0006	4.696	
$3s\rightarrow 2p_{1/2}$	l	2.488	2.492	2.439	2.443	−0.0002	2.442	2.48[b]
	v	2.525	2.491	2.477	2.442	−0.0004	2.442	
$3s\rightarrow 2p_{3/2}$	l	3.519	3.524	3.449	3.455	−0.0003	3.454	3.51[b]
	v	2.572	3.524	3.504	3.454	−0.0006	3.454	
				B ($Z=5$, core $=1s^22s^2$)				
$3s\rightarrow 2p_{1/2}$	l	1.224	1.179	1.148	1.107	0.016	1.124	1.132[c]
	v	0.965	1.179	0.894	1.057	0.038	1.118	
$3s\rightarrow 2p_{3/2}$	l	1.732	1.669	1.625	1.567	0.023	1.590	1.601[c]
	v	1.365	1.669	1.266	1.496	0.054	1.582	

[a]Reference [15].
[b]Reference [16].
[c]Reference [18].

the length and velocity forms. It is crucial to add an infinite set of diagrams generated from the irreducible second-order diagrams to produce GI value. Algebraically, this is equivalent to including $Z^{(2)}_{mn}(\Lambda)$ in Eq. (16) self-consistently. Our numerical results shown in Table I indeed offer numerical evidence of the gauge invariance of Eq. (15). In addition to being GI, our results are in good agreement with the experiment [15,16] and consistent with recent accurate theoretical values of Blundell *et al.* [17] and of Weiss [1]. For Boron, our results agree with recent experimental measurement [18] to within 1%. The accuracy as well as the agreement between the two forms of the transition amplitudes is superior to all previous theoretical results for boron [19].

As we have mentioned earlier, we choose a single energy level for $\Sigma^{(2)}(\omega)$ in solving all Brueckner wave functions with the same κ. An essential requirement for obtaining good approximation to the complete set of the Brueckner wave functions relies on the condition that the absolute values of energy levels of one-particle bound states are much smaller than those of any energy levels of one-hole states. We can simply look at the DF energy spectrum (since we use the DF orbitals to start iteration in solving the Brueckner equation) to see whether the requirement is satisfied or not for a particular atom or ion. The requirement is satisfied for all alkali-metal atoms and for B I. A counter example appears in the boron-isoelectronic sequence. For $Z=6$ in this sequence (namely, C II), the DF energy level of the one-hole state $2s$ is -1.695 a.u. The energy levels of one-particle states $2p_{1/2}$ and $2p_{3/2}$ are -0.865 a.u. and -0.864 a.u., respectively. The term containing the energy denominator of the form [Eq. (5) and Ref. [11]]

$$\varepsilon_v+\varepsilon_{2s}-\varepsilon_{2p_{1/2}}-\varepsilon_{2p_{3/2}}$$

from $\Sigma^{(2)}$ critically depends on the eigenvalue ε_v. It is clear that in the case of C II a single choice of ε_v will not yield a satisfactory spectrum for each κ.

IV. CONCLUSION

We have described a systematic approach to approximate the wave functions and energy levels of many-electron systems with a nondegenerate core plus or minus one electron. The formalism also gives the expression for the transition amplitude between one-particle or one-hole states. The expression has been shown to be gauge invariant (GI) analytically. The approximation scheme can be formulated order by order to meet the required accuracy. The first-order approximation is equivalent to the DF approximation. The second-order approximation is called the Brueckner approximation. In this article, we have used the B-spline method to calculate the transition amplitudes in the Brueckner approximation for the cases of Lithium and Boron. The results of transition amplitudes are in good agreement with experimental measurement. The length and velocity forms agree with each other to within 0.5%.

One of the applications of the Brueckner approximation to atomic systems is reported in Ref. [20]. Other possible applications, such as the calculation of hyperfine structure and parity-violating transitions, is currently under exploration.

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[1] A. W. Weiss, Can. J. Chem. **70**, 456 (1992).
[2] G. W. F. Drake, Can. J. Phys. **66**, 586 (1988).
[3] See, for example, G. Laplanche, M. Jaonen, and A. Rachman, J. Phys. B **16**, 415 (1983).
[4] S. A. Blundell, W. R. Johnson, and J. Sapirstein, Phys. Rev. A **43**, 3407 (1991).
[5] N.Vaeck, M. Godefroid, and C. Froese Fischer, Phys. Rev. A **46**, 3704 (1992).
[6] G. Feldman and T. Fulton, Ann. Phys. **152**, 376 (1984); **172**, 40 (1986).
[7] T. Fulton and W. R. Johnson, Phys. Rev. A **34**, 1686 (1984).
[8] S. S. Liaw, Can. J. Phys. **70**, 644 (1992).
[9] S. S. Liaw, Can. J. Phys. **70**, 1279 (1992).
[10] S. S. Liaw, Phys. Rev. A **47**, 1726 (1993).
[11] S. S. Liaw, Phys. Rev. A **48**, 3555 (1993).
[12] Gy. Csanak, H. S. Taylor, and R. Yaris, Adv. At. Mol. Phys. **7**, 287 (1971).
[13] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many Particle Systems* (McGraw-Hill, New York, 1971).
[14] W. R. Johnson, S. A. Blundell, and J. Sapirstein, Phys. Rev. A **37**, 307 (1988).
[15] A. Gaupp, P. Kuske, and H. J. Andrä, Phys. Rev. A **26**, 3351 (1982).
[16] G. A. Martia and W. L. Wiese, J. Phys. Chem. Ref. Data **5**, 537 (1976).
[17] S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, Phys. Rev. A **40**, 2233 (1989).
[18] T. R. O'Brian and J. F. Lawler, Astron. Astrophys. **255**, 420 (1992).
[19] R. P. McEachran and M. Cohen, J. Quant. Spectrosc. Radiat. Transfer **27**, 111 (1982).
[20] S. S. Liaw (unpublished).