

Combined configuration-interaction and many-body-perturbation-theory calculations of energy levels and transition amplitudes in Be, Mg, Ca, and Sr

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Configuration interaction (CI) calculations in atoms with two-valence electrons, carried out in the $V^{(N-2)}$ Hartree-Fock potential of the core, are corrected for core-valence interactions using many-body perturbation theory (MBPT). Two variants of the mixed CI+MBPT theory are described and applied to obtain energy levels and transition amplitudes for Be, Mg, Ca, and Sr.

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I. INTRODUCTION

Although Be, Mg, Ca, and Sr atoms have been studied theoretically for many years and numerous calculations are available in the literature, energy levels of those divalent atoms have been treated primarily with semiempirical methods and only a limited number of low-lying levels have been evaluated using *ab initio* methods, which often do not provide sufficient precision or require extensive computer resources. Semiempirical methods, to their advantage, do not require significant computer resources and can be applied easily to a large number of levels; however, such theories have limited predictive power and accuracy. Although energies obtained using semiempirical methods agree well with one another and with experiment, oscillator strengths obtained by different semiempirical calculations are inconsistent [1]. Examples of semiempirical calculations can be found for Be in [1], for Ca in [2], and for Sr in [3]. Large-scale *ab initio* configuration interaction (CI) calculations of energies and transition rates, although capable of high accuracy, have been performed only for a few low-lying levels in the Be [4,5] and Mg [6] isoelectronic sequences. The size of the configuration space in such CI calculations is limited by the available computer resources. Smaller-scale CI calculations, carried out in the frozen $V^{(N-2)}$ Hartree-Fock potential of the core, lead to poor results. We found, for example, that frozen-core CI calculations in Ca gave energies so inaccurate that it was difficult, if at all possible, to identify many closely spaced levels of experimental interest. Multiconfiguration Dirac-Fock (MCDF) and Hartree-Fock (MCHF) methods have also been used to obtain energies and oscillator strengths in divalent atoms: MCHF for Be-like ions [7] and neutral calcium [8], and MCDF for Mg-like ions [9]. The accuracy of MCHF and MCDF calculations in neutral atoms is poor, basically because of computational limits on the number of configurations. Polarization potentials have been used in conjunction with MCHF calculations [10] to improve the accuracy of energies for Ca I and Ca II. Many-body per-

turbation theory (MBPT) calculations of energies and oscillator strengths for neutral divalent atoms using an effective Hamiltonian within a small model space, are also found to be inaccurate [11,12]. Good agreement with experiment for divalent atoms, however, was achieved in Refs. [13–15] with a combined CI+MBPT method. A related method was applied to calculations of energies and oscillator strengths for Mg-like ions in Ref. [16]. Among the *ab initio* methods, CI+MBPT is particularly attractive since it is capable of giving accurate energies and transition rates for both light and heavy divalent atoms with modest computer resources.

A precise and efficient theoretical method for calculations of properties of divalent atoms is needed for many possible applications of current interest, including calculations of spectra, transition amplitudes, hyperfine structure constants, polarizabilities, parity-nonconserving amplitudes, van der Waals coefficients, and Lennard-Jones coefficients. There is also growing interest in properties of divalent atoms in conjunction with low-temperature Bose-Einstein condensation (BEC) experiments. For example, the prospect for achieving BEC in divalent atoms was discussed in [17,18] and depends on the size of the van der Waals coefficient.

At least two major difficulties have been recognized in studying divalent atoms. First, core-polarization effects are significant and must be taken into account. A similar situation exists in monovalent atoms where various methods have been successfully applied to describe the valence-core interaction. We have made extensive use of one of these methods, MBPT, and have developed methods for calculating all diagrams up to the third order for energies [19] and transition amplitudes [20]. A second major difficulty is that two valence electrons interact so strongly in neutral atoms that two-particle diagrams must be included to infinite order. Since infinite order is required, the MBPT method is difficult to apply. However, valence-valence correlations can be accounted for completely using the CI method.

With this in mind, we have developed a method (similar to that used in Refs. [13–15] but with important differences) for high-precision calculations of properties of atoms with two-valence electrons. The method starts with a complete CI calculation of the interactions between the valence electrons in a frozen core and accounts for valence-core interactions using MBPT. We apply this combined CI+MBPT method to calculate energy levels and transition amplitudes for Be, Mg, Ca, and Sr.

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II. METHOD

A. Frozen-core CI

We start with a lowest-order description of a divalent atom in which the closed $N-2$ electron core is described in the HF approximation and valence or excited electrons satisfy HF equations in the “frozen” $V^{(N-2)}$ HF core. As we mentioned in the introduction, the strong valence-valence correlations must be included to infinite order; the CI method accomplishes this. The configuration space for divalent atoms is built up in terms of the excited HF orbitals. We include all orbitals with angular momentum $l \leq 5$ (partial-wave contributions scale as $1/(l+1/2)^4$) and we use 25 basis functions out of a complete set of 40 for each value of angular momentum. The effect of these restrictions is insignificant considering the perturbative treatment of valence-core correlations.

A detailed discussion of the CI method (as used here) can be found in Ref. [21]. We introduce a configuration-state wave-function $\Phi_I \equiv \Phi_{JM}(ij)$ in which single-particle basis orbitals i and j are combined to give a two-particle wave-function with angular momentum J and definite parity. We then expand the general two-particle wave function Ψ_{JM} in terms of all $\Phi_{JM}(ij)$ in our basis set

$$\Psi_{JM} = \sum_I c_I \Phi_I. \quad (2.1)$$

The expectation value of the Hamiltonian becomes

$$\langle \Psi_{JM} | H | \Psi_{JM} \rangle = \sum_I E_I c_I^2 + \sum_{I,K} V_{IK} c_I c_K, \quad (2.2)$$

where $E_I = \epsilon_i + \epsilon_j$ is the sum of single-particle HF energies and V_{IK} is a first-order, two-particle correlation matrix element (see, for example, [21]) between the configurations $I = (ij)$ and $K = (kl)$. The variational condition leads to CI equations

$$\sum_K (E_I \delta_{IK} + V_{IK}) c_K = \lambda c_I, \quad (2.3)$$

from which CI energies (λ) and wave functions ($\sum_I c_I \Phi_I$) are found.

B. Combining CI with MBPT

Core-polarization effects can be treated using MBPT. In this paper, we introduce two procedures that enable us to combine frozen-core CI and second-order two-valence-electron MBPT, which we refer to as “CI averaging” and “Brueckner-orbital CI” methods.

1. CI averaging

In this first method, the core-valence interaction ΔE_{vc} is obtained by “averaging” MBPT corrections over CI wave functions

$$\Delta E_{vc} = \sum c_I c_K \langle \Phi_I | H^{(2)} | \Phi_K \rangle, \quad (2.4)$$

where the configuration weights c_I and c_K are taken from the solution of the CI equation, Eq. (2.3), and $H^{(2)}$ is that part of the effective Hamiltonian projected onto the valence electron subspace containing second-order valence-core interactions. The dominant second-order parts of the effective Hamiltonian, beyond those accounted for in the CI calculation, are the screening and self-energy diagrams: $H^{(2)} = H^{\text{screen}} + H^{\text{self}}$, the self energy being much larger than the screening and both being larger than the remaining second-order terms.

We borrow ready-to-use formulas, derived using standard techniques, from Ref. [12]. The screening contribution to the effective Hamiltonian is

$$\begin{aligned} H_{v'w'vw}^{\text{screen}} &= -\eta_{v'w'} \eta_{vw} \sum_{\alpha' \beta' \alpha \beta} C_1(\alpha' \beta' \alpha \beta) \\ &\times \sum_{nbk} \frac{(-1)^{j_{w'} + j_v + j_n + j_b}}{[k]} \begin{Bmatrix} j_{\alpha'} & j_{\beta'} & J \\ j_{\beta} & j_{\alpha} & k \end{Bmatrix} \\ &\times \frac{Z_k(\alpha' b \alpha n) Z_k(\beta' n \beta b)}{\epsilon_{\beta} + \epsilon_b - \epsilon_{\beta'} - \epsilon_n}, \end{aligned} \quad (2.5)$$

where

$$\begin{aligned} C_1(\alpha' \beta' \alpha \beta) &= (-1)^J [\delta_{\alpha' v'} \delta_{\beta' w'} \delta_{\alpha v} \delta_{\beta w} \\ &+ \delta_{\alpha' w'} \delta_{\beta' v'} \delta_{\alpha v} \delta_{\beta w}] + \delta_{\alpha' v'} \delta_{\beta' w'} \delta_{\alpha w} \delta_{\beta v} \\ &+ \delta_{\alpha' w'} \delta_{\beta' v'} \delta_{\alpha w} \delta_{\beta v}. \end{aligned} \quad (2.6)$$

The self-energy contribution to $H^{(2)}$ is

$$\begin{aligned} H_{v'w'vw}^{\text{self}} &= \eta_{v'w'} \eta_{vw} [\delta_{w'w} \Sigma_{v'v} + \delta_{v'v} \Sigma_{w'w} \\ &+ (-1)^J (\delta_{v'w} \Sigma_{w'v} + \delta_{w'v} \Sigma_{v'w})], \end{aligned} \quad (2.7)$$

where

$$\begin{aligned} \Sigma_{ij}(\epsilon_0) &= \sum_{kcmn} \frac{(-1)^{j_m + j_n - j_i - j_c}}{[j_i][k]} \frac{X_k(icmn) Z_k(mn jc)}{\epsilon_0 + \epsilon_c - \epsilon_m - \epsilon_n} \\ &+ \sum_{kbcn} \frac{(-1)^{j_i + j_n - j_b - j_c}}{[j_i][k]} \frac{X_k(inbc) Z_k(bc jn)}{\epsilon_0 + \epsilon_n - \epsilon_b - \epsilon_c}. \end{aligned} \quad (2.8)$$

In the above equations, J is the angular momentum of the coupled two-particle states. The coupled radial integrals $X_k(abcd)$ and $Z_k(abcd)$ are defined in [12]. We use the notation $[k] = 2k + 1$. The quantities η_{vw} are normalization constants, $\eta_{vw} = 1/\sqrt{2}$ for identical particle states and 1, otherwise. In the expression for the self energy, the angular momenta of the i th and j th orbitals satisfy $\kappa_i = \kappa_j$, where $\kappa_i = \mp(j_i + 1/2)$ for $j_i = l_i \pm 1/2$ is the angular quantum number uniquely specifying the spinor for state i . Since we found that the second-order self-energy correction is very important, we also consider the fourth-order self-energy obtained by iteration

$$\Sigma_{ij}(\epsilon_0) \rightarrow \Sigma_{ij}(\epsilon_0) + \sum_{k \neq i} \frac{\Sigma_{ik}(\epsilon_0)\Sigma_{kj}(\epsilon_0)}{\epsilon_i - \epsilon_k}. \quad (2.9)$$

In heavy atoms, the choice of ϵ_0 deserves special consideration. Problems with denominators arise from the fact that single-particle orbitals used in the self-energy calculation are not optimal, in the sense that there is mutual interaction between valence electrons not accounted for, even approximately, in the $V^{(N-2)}$ potential and accounted for excessively in the $V^{(N)}$ potential which is used, for example, in Ref. [14]. One practical solution to this problem is to use “optimized” denominators [14]. A consistent theory requires an *ab initio* treatment of the denominator problem. Basing calculations of atoms with two-valence electrons on a more realistic potential can reduce uncertainties in the choice of the denominator in the self-energy corrections.

We calculated energies of several levels using the CI averaging method and found that the best agreement with experiment for Be and Mg was obtained with ϵ_0 equal to 1/2 of the CI energy. For the case of Ca, the best agreement was obtained choosing ϵ_0 between 1/2 and one times the CI energy. One advantage of the CI averaging method is that the basic CI code is simple and that the CI wave functions can be stored and used many times. A cutoff condition can be imposed, as a compromise between speed and accuracy. The fastest approximation (giving the poorest accuracy) is obtained by restricting the MBPT corrections to the leading configurations. We used this leading configuration approximation to estimate the magnitude of the core-excitation effects as the first step in developing our computer code. Adjusting the cutoff condition, we readily reached a high level of accuracy (finally we chose the cutoff condition $|c_I c_K| < 0.002$ for all calculations). The energies for several states of Be, Mg, and Ca presented in this paper have been calculated with the CI averaging method. The principal drawback of this method is that wave functions necessary for calculations of other properties are not automatically obtained.

2. Brueckner-orbital CI

The effective Hamiltonian formalism [12] leads to the problem of diagonalizing the Hamiltonian matrix built on the frozen-core two-electron configuration state functions Φ_I . We split this matrix into functionally distinct pieces,

$$H = H^{(0)} + H^{(1)} + H^{(2)}, \quad (2.10)$$

where $H^{(0)}$ is the zeroth-order Dirac-Fock Hamiltonian, which in the Dirac-Hartree-Fock (DHF) basis is

$$H_{v'w'vw}^{(0)} = \delta_{vv'} \delta_{ww'} (\epsilon_v^0 + \epsilon_w^0),$$

and $H^{(1)}$ is the first-order electron-electron interaction Hamiltonian

$$H_{v'w'vw}^{(1)} = V_{v'w'vw}^{(1)},$$

defined in Ref. [12]. $H^{(2)}$ is the second-order correction which consists of the two-particle screening correction and the one-particle self-energy correction defined previously. In

the CI averaging method, $H^{(0)} + H^{(1)}$ is diagonalized first in a DHF basis (where $H^{(0)}$ is diagonal) to give state energies and CI wave functions, then $H^{(2)}$ is evaluated using the CI wave functions to give corrections for the core-valence interaction.

In the Brueckner-orbital (BO)-CI method, the basis functions are chosen as orthonormal solutions of the quasiparticle equation,

$$[h_0 + V_{\text{HF}} + \Sigma_{ij}(\epsilon)] \phi_j = \epsilon^{BO} \phi_i. \quad (2.11)$$

In this BO basis,

$$(H^{(0)} + H^{\text{self}})_{v'w'vw} = \delta_{vv'} \delta_{ww'} (\epsilon_v^{BO} + \epsilon_w^{BO}). \quad (2.12)$$

The basis orbitals include second-order self-energy corrections together with the lowest-order DHF potential. The residual nontrivial part of the effective Hamiltonian in the BO basis is the sum $H^{(1)} + H^{\text{screen}}$. In the Brueckner orbital-CI method, the residual Hamiltonian matrix is evaluated in the BO basis and diagonalized to obtain state energies and CI wave functions. The BO-CI method is equivalent to CI averaging method if we neglect energy differences in the denominators of H^{self} and H^{screen} (of order of the valence-valence interaction energy), which are small compared to the core excitation energies. The BO-CI method is also equivalent to the effective Hamiltonian method in [14] to the same level of precision, provided all second-order diagrams are included. Some advantage is gained in accuracy compared to the CI averaging method, since the largest valence-core corrections [those from $\Sigma_{ij}(\epsilon_0)$] are taken into account to infinite order.

The Brueckner-orbital CI method is very convenient for calculations of transition amplitudes; once the residual interaction is diagonalized, the associated wave functions are immediately available. We include random-phase approximation (RPA) corrections in calculations of transition amplitudes by replacing “bare” matrix elements with “dressed” elements as explained in [20]. Length-form and velocity-form dipole matrix elements are found to be in close agreement in BO-CI calculations that include RPA corrections.

III. CALCULATIONS OF SPECTRA USING CI AVERAGING

The CI averaging method is fast and convenient for calculations of energies when a large number of levels are needed, especially at the stage of adjusting the code parameters. Below, we present our calculations for many levels of Be, Mg, and Ca atoms to demonstrate the accuracy of this method. We evaluate the valence-core correction ΔE_{vc} to the CI energy using a subset of the CI coefficients limited to those satisfying $|c_I c_K| \leq 0.002$. The parameter ϵ_0 in the self energy was chosen to be $\epsilon_{\text{CI}}/2$ for Be and Mg. For calcium it was increased to $3\epsilon_{\text{CI}}/4$ to obtain better agreement for energies of the $4p^2$ states.

The basis set used to set up the calculations consisted of 25/40 DHF basis functions for each value of $l \leq 5$. The basis functions were formed as linear combinations of *B* splines of order 7, constrained to a cavity of radius $R = 80 a_0$.

TABLE I. Comparison of CI-averaging energy levels (cm^{-1}) of Be I with experimental data from the NIST database [22].

Configuration	Term	J	NIST	CI average
$2s^2$	$1S$	0	0	0
$2s2p$	$3P^o$	0	21978	21996
$2s2p$	$3P^o$	2	21981	22000
$2s3s$	$3S$	1	52081	52074
$2p^2$	$1D$	2	56882	56890
$2s3p$	$3P^o$	1	58907	58890
$2s3p$	$3P^o$	2	58908	58896
$2p^2$	$3P$	1	59695	59749
$2p^2$	$3P$	2	59697	59747
$2s3d$	$3D$	3	62054	62033
$2s3d$	$1D$	2	64428	64414
$2s4s$	$3S$	1	64506	64528
$2s4s$	$1S$	0	65245	65261
$2s4p$	$3P^o$	2	66812	66792
$2s4d$	$3D$	3	67942	67924
$2s4f$	$3F^o$	3	68241	68224
$2s4f$	$1F^o$	3	68241	68224
$2s4d$	$1D$	2	68781	68774
$2s5s$	$3S$	1	69010	69056

A. Calculations for Be

We chose to study a Be atom for several reasons. First, this atom has a small core and, consequently, requires relatively little computation time. Second, because of the small size of the core-valence interaction, calculations for Be are expected to be very precise.

A comparison of the resulting CI energies with measured energies from the National Institute of Standards and Technology (NIST) database [22] is shown in Table I. This comparison provides the first test of the CI averaging method. The values listed in the table agree with experiment at the level of tens of cm^{-1} . The residual deviation can be explained as neglect of small Coulomb and Breit diagrams, which will be the subject of future investigations.

It is also interesting to compare CI energies, with and without the MBPT corrections ΔE_{vc} , with energies from the NIST database. Such a comparison is given in Table II and illustrates the importance of the valence-core corrections.

The agreement with experiment improves by an order of magnitude for the CI-averaging method as compared with a frozen-core CI calculation. Indeed, we found it necessary to use the more precise energies obtained from the CI-averaging method to properly identify the transitions shown in this table.

TABLE II. Comparison of frozen-core CI energies (cm^{-1}) and CI-averaging energies for Be I with experimental energies from the NIST database [22].

Configuration	Term	J	NIST	CI average	Difference	Frozen CI	Difference
$2s3s$	$1S$	0	54677	54664	-13	54509	168
$2p^2$	$3P$	0	59694	59737	43	60090	-396
$2s5s$	$1S$	0	69322	69307	-15	69387	+65

B. Calculations for Mg

Another example where the CI averaging method predicts energy levels accurately is magnesium. In this atom, however, core correlations are larger and the treatment of the valence-core interaction term requires more careful analysis. One important aspect is choosing the parameter ϵ_0 in the denominators of the MBPT corrections, another is the treatment of self-energy diagrams. We found mild sensitivity of final energies in Mg to the choice of ϵ_0 . The corrected energies shown in the column headed “CI + 2nd” in Table III, which were obtained with the choice $\epsilon_0 = \epsilon_{CI}/2$, are seen to be in close agreement with experimental energies [22].

Typically, the self-energy correction is much larger than other valence-core diagrams; for example, in the Mg ground state, the self energy is -1.65×10^{-2} a.u. while the screening contribution is ten times smaller, 1.83×10^{-3} a.u. Valence-core contributions in fourth order, obtained by iterating (or chaining) the second-order Brueckner corrections are also found to be significant, -6.57×10^{-4} a.u. for the Mg ground state. The effect of including corrections from chaining the self energy shown in the column headed “CI + 4th” in Table III is seen to further improve the agreement with experiment.

C. Ca atom

In Table IV, several even parity $J=0$ levels are calculated with the frozen-core CI and CI-averaging methods. Compared to the frozen-core CI method, the agreement is significantly improved with the addition of MBPT corrections, changing the difference between experiment and theory from approximately one thousand cm^{-1} to a few hundred cm^{-1} . This significant change clearly indicates the importance of the valence-core interaction, which is much stronger than in the case of Be and Mg. As a result, the final accuracy of the CI+MBPT method is also lower than for the lighter atoms. While the poor accuracy of frozen CI energies prevents the identification of energy levels, more accurate CI+MBPT energies permit one to identify many Ca levels. It is interesting to notice that the sequence of experimental levels for the states of a particular symmetry is the same as the sequence of theoretical eigenvalues. Once the question of classification is solved, various properties of atoms can be calculated using, for example, frozen-core CI.

In the case of Ca, another problem that needs attention is the choice of the parameter ϵ_0 in the self energy, the dominant part of the core-valence interaction. We find that there is an optimal value of this parameter between $\epsilon_{CI}/2$, our standard value for Be and Mg, and ϵ_{CI} , for which the ground state becomes very accurate. In Table IV we chose this pa-

TABLE III. Comparison of energies (a.u.) in Mg obtained from frozen-core CI, CI averaging with second-order self-energy, and CI averaging with chained fourth-order self-energy, with experimental energies from the NIST database [22].

Configuration Level	CI	CI+2nd	CI+4th	Experiment	Δ (cm ⁻¹)
$3s^2^1S_0$	0.818	0.8329	0.833513	0.833518	1
$3s4s^1S_0$	0.624	0.6349	0.635260	0.635303	9
$3s5s^1S_0$	0.583	0.5938	0.594240	0.594056	40
$3s6s^1S_0$	0.566	0.5772	0.577813	0.577513	66
$3p^2^3P_0$	0.562	0.5695	0.569747	0.570105	79
$3s3p^3P_1$	0.723	0.7336	0.733991	0.733869	27
$3s3p^1P_1$	0.661	0.6733	0.673673	0.673813	31
$3s4p^3P_1$	0.604	0.6156	0.615834	0.651524	68
$3s4p^1P_1$	0.597	0.6086	0.608606	0.608679	16
$3s3p^3P_2$	0.723	0.7333	0.733867	0.733684	67

parameter to be $0.75\epsilon_{CI}$. In the following section, we will illustrate our calculations of transition amplitudes for several levels of Mg, Ca, and Sr where other precise calculations and measurements exist.

IV. CALCULATIONS USING THE BRUECKNER-ORBITAL CI METHOD

In this section, we present our calculations of energies and transition amplitudes with the Brueckner-orbital CI method. Our basis consisted of $25 V_{HF}^{N-2}$ orbitals (those orbitals were constructed from 40 B splines in a cavity of radius 80 a.u.), in which 14 lowest excited states were replaced with Brueckner orbitals. The resulting one-valence electron energies for the divalent atoms were tested by comparing with experimental energies for the corresponding monovalent ions. For Mg^+ , the BO energies agree with experiment better than do the second-order energies (Table V). A second iteration of the BO equation was also included in the CI-averaging method (Table III) to improve accuracy. The small size of the residual deviation from experiment in both tables can be attributed to higher-order diagrams. Two-particle screening corrections with the restriction $n < 15$ were included in the effective Hamiltonian, diagonalization of which provided the initial and final state wave functions necessary for the calculation of transition amplitudes. We checked that restrictions on the number of BO and screening diagrams included in the calculation did not lead to significant errors. Dressed transi-

tion amplitudes were used to take into account RPA corrections, which provide better length- and velocity-form agreement. We completely neglected the extremely time consuming structural radiation corrections which are expected to be small for the length form; for this reason, the result calculated in length form should be considered as more accurate. Small normalization corrections are also omitted.

A. Be case

The most accurate results for divalent atoms are expected for Be since it contains the smallest MBPT corrections. In Table VI, we compare our calculations with available precise calculations and experiment. Transition energies agree with experiment to better than 0.1%, except for the transition $2s3s^1S-2s2p^1P$ which has 0.4% accuracy. Our oscillator strengths agree well with those obtained in very accurate *ab initio* calculations of Ref. [23] and in semiempirical calculations of Ref. [1] that reproduce energies very closely; for the principal transition $2s2^1S-2s2p^1P$, our value 1.375 differs by one in the fourth digit from the value 1.374 in Ref. [23], the accuracy being better than 0.1%, and coincides with the value of Ref. [1]. Very close agreement with *ab initio* theory is also achieved for the transition $2s3s^1S-2s3p^1P$. For suppressed transitions, an accuracy of 1% is obtained. Conducting a simple statistical analysis, we found that energy differences in the CI averaging and BO-CI calculations have similar statistical errors, but slightly different systematic

TABLE IV. Comparison of the accuracy of frozen-core CI and CI averaging calculations for Ca. The parameter $\epsilon_0 = 0.75\epsilon_{CI}$.

Configuration	Level	Frozen CI	Difference	CI-average	Difference	Experiment
$4s5s$	1S_0	31901	-1416	33196	-121	33317
$4p^2$	3P_0	36699	-1718	38900	483	38418
$4s6s$	1S_0	39376	-1314	40504	-186	40690
$4p^2$	1S_0	41480	-306	42366	580	41786
$4s7s$	1S_0	42673	-1604	43841	-436	44277
$4s8s$	1S_0	44277	-1610	45551	-336	45887
$4s9s$	1S_0	45629	-1206	46912	77	46835

TABLE V. Comparison of DHF spline energies “DHF,” second-order energies, and energies resulting from diagonalization of the self-energy matrix, Brueckner-orbital “BO” energies, with experiment for the Mg^+ ion. The core configuration is $1s^2 2s^2 2p^6$. The size of the self-energy matrix is 14×14 for each angular momentum. All energies are expressed in cm^{-1} .

States	DHF	second order	BO	Experiment
$3s_{1/2}$	118825	121127	121184	121268
$4s_{1/2}$	50858	51439	51446	51463
$5s_{1/2}$	28233	28467	28469	28477
$3p_{1/2}$	84295	85508	85542	85598
$4p_{1/2}$	40250	40625	40633	40648
$5p_{1/2}$	23642	23808	23811	23812

shifts which can be explained partially by different denominators in the two methods. Another reason is the cut-off condition 0.002 in the former method and restriction on the number of Brueckner orbitals in the latter. The effect of the partial-wave restriction on the ground-state energy in both methods is 6 cm^{-1} . If this value is accounted for, the agreement becomes slightly better. The results in our tables are not extrapolated owing to the smallness of the omitted partial-wave contributions.

TABLE VI. Comparison of the present transition energies ω (a.u.) and oscillator strengths f for Be with those from other theories and experiment. A few allowed singlet-singlet transitions of the type S_0 - P_1^o between low-lying states are considered. The experimental uncertainties are given in parentheses.

Transition	Source	ω (theory)	ω (experiment)	f
$2s^2$ - $2s2p$	Present	0.194126	0.193954	1.3750
	[24]			1.38(0.12)
	[25]			1.34(0.05)
	[1]	0.19412		1.375
	[23]	0.193914		1.374
	[26]			1.3847
	[27]			1.470
	[28]			1.375
$2s^2$ - $2s3p$	Present	0.274231	0.274251	0.00904
	[1]	0.27441		0.00901
	[23]	0.274236		0.00914
	[26]			0.0104
	[27]			0.037
	[7]			0.00885
$2s3s$ - $2s2p$	Present	0.054977	0.05519	0.1188
	[1]	0.05509		0.118
	[23]	0.055198		0.1175
	[26]			0.1199
	[27]			0.140
$2s3s$ - $2s3p$	Present	0.025128	0.025107	0.9557
	[24]	0.0252		0.958
	[23]	0.025124		0.9565
	[26]			0.9615

TABLE VII. Comparison of BO-CI energies (cm^{-1}) with experiment for Mg, Ca, and Sr.

Levels	Theory	Experiment	Difference
Mg atom			
$3s4s \ ^1S_0$	43452	43503	-51
$3s5s \ ^1S_0$	52517	52556	-39
$3s6s \ ^1S_0$	56154	56187	-33
$3s3p \ ^3P_1$	21834	21870	-44
$3s3p \ ^1P_1$	35059	35051	8
$3s4p \ ^3P_1$	47806	47844	-38
$3s4p \ ^1P_1$	49317	49347	-30
Ca atom			
$4s5s \ ^1S_0$	33505	33317	188
$4p^2 \ ^3P_0$	38651	38418	233
$4s6s \ ^1S_0$	40862	40690	172
$4s4p \ ^3P_1$	15595	15210	385
$4s4p \ ^1P_1$	23797	23652	145
$4s5p \ ^3P_1$	36760	36555	205
$4s5p \ ^1P_1$	36917	36732	185
Sr atom			
$5s6s \ ^1S_0$	30874	30592	282
$5p^2 \ ^3P_0$	35913	35193	720
$5p^2 \ ^1P_0$	37696	37160	536
$5s5p \ ^3P_1$	15081	14504	577
$5s5p \ ^1P_1$	21981	21699	282
$5s6p \ ^3P_1$	34293	33868	425
$5s6p \ ^1P_1$	34512	34098	414

B. The cases of Mg, Ca, and Sr

The accuracy of both the CI averaging and the BO-CI calculations considered above decreases from light to heavy divalent atoms. Table VII illustrates this tendency in BO-CI calculations: for Mg, the theory-experiment differences range within 50 cm^{-1} , similar to what we have in Table III, and for Ca the deviation from experiment increases to about 200 cm^{-1} which is comparable to that in Table IV. The lowest accuracy is for Sr, which has the largest core and MBPT corrections. Similar results for energies have been obtained in Ref. [14]. Our experiment-theory differences exhibit a systematic shift, which if subtracted, brings results into better agreement. For example, in Ca this shift is 216 cm^{-1} . After its subtraction, the residual deviation is 73 cm^{-1} . This subtraction procedure can be used in cases where closely spaced levels are difficult to identify. The systematic shift can be attributed to omitted correlations that affect mostly the ground state which is used as a reference. The cutoff condition in the CI-averaging method and restrictions on the number of BO and screening diagrams also has some effect on the accuracy of our results. This is one reason why the two methods give slightly different energies. In future development of our computer code, we will try to remove such restrictions completely. Another reason why the two methods give different results is that the choices of ϵ_0 were different. In Table VIII, we illustrate our calculations of transition amplitudes for Mg, Ca, and Sr. All of our transition amplitudes completely agree with those of recent CI+MBPT

TABLE VIII. Comparison of our length form (L) and velocity form (V) calculations with those from Ref. [14] and with experiment.

	Mg	Ca	Sr
	$^1P_1^o(nsnp)-^1S_0(ns^2)$		
L	4.026	4.892	5.238
V	4.019	4.851	5.212
Other ^a	4.03(2)	4.91(7)	5.28(9)
Experiment	4.15(10) ^b	4.967(9) ^e	5.57(6) ^f
	4.06(10) ^c	4.99(4) ^f	5.40(8) ^h
	4.12(6) ^d	4.93(11) ^g	
	$^3P_1^o(nsnp)-^1S_0(ns^2)$		
L	0.0063	0.0323	0.164
V	0.0070	0.0334	0.166
Other ^a	0.0064(7)	0.034(4)	0.160(15)
Experiment	0.0053(3) ⁱ	0.0357(4) ^l	0.1555(16) ^o
	0.0056(4) ^j	0.0352(10) ^m	0.1510(18) ^m
	0.0061(10) ^k	0.0357(16) ⁿ	0.1486(17) ^p

^aPorsev *et al.* [14].

^bLiljeby *et al.* [29].

^cLundin *et al.* [30].

^dSmith and Gallagher [31].

^eZinner *et al.* [18].

^fKelly and Mathur *et al.* [32].

^gHansen [33].

^hParkinson *et al.* [34].

ⁱGodone and Novero [35].

^jKwong *et al.* [36].

^kMitchell [37].

^lHusain and Roberts [38].

^mDrozdowski *et al.* [39].

ⁿWhitkop and Wiesenfeld [40].

^oHusain and Schifino [41].

^pKelly *et al.* [42].

calculations by Porsev *et al.* [14], and are close to experimental values. Length-form and velocity-form amplitudes agree to better than 1% for allowed transitions. Forbidden transitions are more problematic, owing to cancellation effects, and have poorer agreement between gauges and with experiment. The inclusion of the Breit interaction and negative-energy contributions, which are more important for the velocity form, might improve the situation. We also noticed that, if the balance between states such as $p_{1/2}$ and $p_{3/2}$

in relativistic basis is not properly maintained, the results for nonrelativistically forbidden transitions will be unstable. In addition, those transitions were affected by the number of BO and screening diagrams included in calculations. To minimize or exclude those effects in the BO-CI method, the BO orbitals and cut-off conditions were made completely symmetric with respect to $l+1/2$ and $l-1/2$ orbitals and included BO and screening corrections with the number of excited orbitals less than 15.

V. SUMMARY AND CONCLUSION

In this paper, we have introduced two methods to improve the accuracy of the frozen-core CI calculations using MBPT: the CI-averaging method and the Brueckner-orbital CI method. We have applied these methods to Be, Mg, Ca, and Sr atoms. Our calculated energies and transition amplitudes for those atoms are in close agreement with the results of the best available theories and experiments. Compared to semiempirical theories, our method has an advantage in accuracy, and compared to other *ab initio* theories, an advantage of simplicity. These two methods can also be used to evaluate properties of Rydberg states for which only semiempirical calculations exist. Further improvement in accuracy is possible and is being pursued. This theory can be extended easily to treat particle-hole excited states of closed-shell atoms, atoms with three valence electrons, and other more complicated systems.

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